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# **Hydrosilylative reduction of aldehydes and other groups by halosilanes using nucleophiles and ionic liquids as promoters**

A Thesis submitted for the Degree of  
**DOCTOR OF PHILOSOPHY**

**The Open University**  
**2003**

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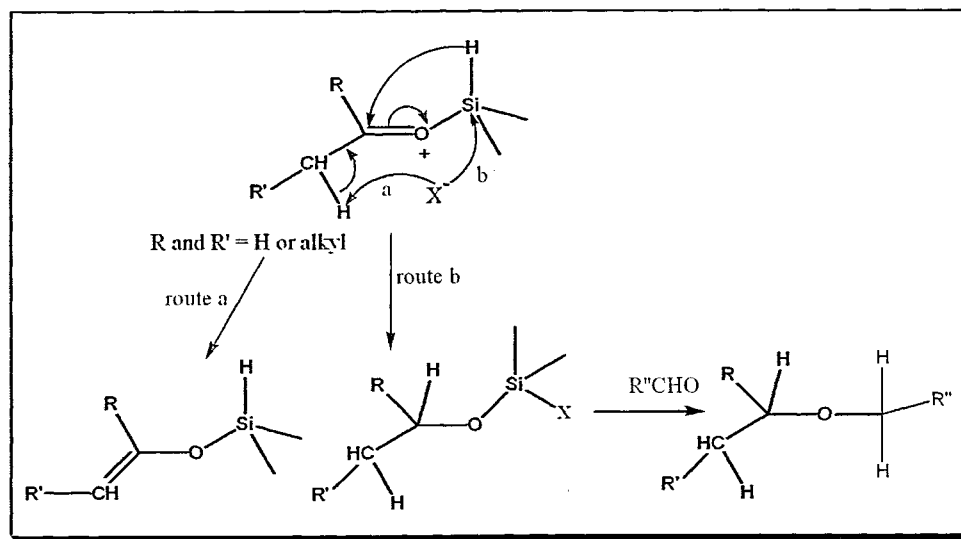
## Abstract

The reduction of aldehydes using hydrosilanes and nucleophiles (TBAX where X = OTf, Br, Cl and I, NMI, polymer amberlysts) gave only symmetric and mixed ethers as products and permitted an alternative to the Williamson synthesis. The yield of the reduction depended on the nature of the salt, the silane and also the aldehyde used.

The efficiency of the salts for the reduction is in the following order: OTf > Br > Cl >

I. We also proved that the efficiency of the silanes is:

$\text{Me}_2\text{HSiOTf} > \text{Me}_2\text{HSiCl}$ . For the aldehydes, bulky alkyl groups slowed down the reduction. The attempted reduction of ketones only gave the enol product. This could be explained by the following Scheme



Route *b* is predominant in the reduction of aldehydes, but route *a* is predominant in the reduction of ketones. For the aldehydes, proton transfer occurs easily and faster than proton abstraction from  $\text{CH}_2$  to give the enol product, which occurred in the ketones due to steric hindrance.

However, due to the presence of salts soluble in the organic phase, the separation of products from reactants remained problematic. Ionic liquids are receiving an upsurge of interest as green solvents, primarily as replacements for conventional media in chemical processes. The reduction of aldehydes using ionic liquids as both solvent and source of anions also gave dialkyl ethers in good yields.

Studies of the hydrosilylation of alkenes and other nucleophilic reactions, such as bromination and the Peterson reaction, showed that different products and isomer ratios are obtained using conventional organic media compared with ionic liquids. Ionic liquid and the presence of the phenyl group as a substituent on the alkenes encourage the formation of the  $\alpha$ -product (Markownikov product). The nature of the silane,  $(\text{EtO})_3\text{SiH}$  and  $\text{Et}_3\text{SiH}$ , does not greatly affect the  $\alpha$ - to  $\beta$ - ratio of the products. The yields of  $\alpha$ - and  $\beta$ - products obtained are in the range of 30-50 %.

The Peterson reaction was not successful with only starting material being recovered; the ionic liquid is not nucleophilic enough to cause the cleavage of the silicon-carbon bond, which allows the formation of the  $\beta$ -silylcarbanion.

**Cette thèse est spécialement dédiée à mes mamies:**

**Mme Bonnevialle Gabrielle**

**Mme Silanus Philomène**

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## Table of Contents

	page
<b>Chapter 1-Background to organosilicon compounds</b>	<b>1-24</b>
1.1-Properties of organosilanes	1
1.2-Nomenclature of organosilicon compounds	3
1.3-Analytical and spectroscopic techniques for silicon compounds	5
1.4-Reactivity of the Si-H bond	7-24
1.4.1-Formation by substitution of a trifunctional organosilane.	8
1.4.2-Neutral donation to an organosilane	12
1.4.3-Co-ordination of anions to tetracoordinate silicon compounds	16
1.5-Conclusions	24
 <b>Chapter 2- Reductions of carbonyl compounds by hydrosilanes activated by nucleophiles</b>	 <b>25-99</b>
2.1-Reduction of aldehydes with $\text{Me}_2\text{HSiOTf}$ in chloroform	26
2.1.1-Reduction of benzaldehyde	26
2.1.2-Reduction of octanal	27
2.1.3-Reduction of trimethylacetaldehyde	27
2.1.4-Reduction of 2-methylbutanal	27
2.1.5-Mechanism of reduction of aldehydes by $\text{Me}_2\text{HSiOTf}$	28
2.2-Reduction of aldehydes with $\text{Me}_2\text{HSiOTf}$ in chloroform in the presence of salts ( $\text{Bu}_4\text{N}^+\text{Y}^-$ where $\text{Y}=\text{OTf}$ )	28
2.2.1 Reduction of benzaldehyde	28
2.2.2-Reduction of octanal	30
2.2.3-Reduction of trimethylacetaldehyde	30
2.2.4-Reduction of 2-methylbutanal	30
2.2.5-Conclusions	31
2.2.6-Mechanism of the reduction reactions	31
2.3-Reduction of aldehydes with $\text{Me}_2\text{HSiOTf}$ in the presence of $\text{Bu}_4\text{N}^+\text{Y}^-$ ( $\text{Y} = \text{Br}^-, \text{Cl}^-, \text{I}^-$ ) in chloroform	33
2.4-Reduction of aldehydes with $\text{Me}_2\text{HSiX}$ where $\text{X}=\text{chloride}$ in chloroform	34
2.4.1-Reduction of benzaldehyde	34
2.4.2-Reduction of others aldehydes	35
2.5-Reduction of a mixture of two different aldehydes with $\text{Me}_2\text{HSiOTf}$ in the presence of nucleophiles in chloroform	36
2.5.1-Reduction of benzaldehyde and hexanal	37
2.5.2-Reduction of benzaldehyde and octanal	39



2.5.3-Reduction of others aldehydes	41
<b>2.6-Reduction of aldehyde and alcohol together in the presence of Me<sub>2</sub>HSiX and salt</b>	42
<b>2.7-Reaction of a dialkoxysilane with a nucleophilic salt</b>	45
<b>2.8-Reduction of an aldehyde in the presence of an alkoxyhydrosilane</b>	47
2.8.1-Reduction of benzaldehyde using dimethylbutoxysilane	48
2.8.2-Reduction of a range of aldehydes using alkoxyhydrosilanes	50
<b>2.9-Reduction of aldehydes with Me<sub>2</sub>HSiX where X= OTf, Cl in chloroform in the presence of an Amberlyst resin</b>	51
2.9.1 -Reduction of aldehydes using bromide Amberlyst polymers and silanes as reducing agent	51
2.9.2 -Reduction of aldehydes using chloride Amberlyst polymer	53
<b>2.10-Reduction of ketones, R<sub>1</sub>R<sub>2</sub>C=O, with Me<sub>2</sub>HSiOTf in chloroform under different conditions.</b>	55
2.10.1-Reduction of ketones with Me <sub>2</sub> HSiOTf in chloroform	55
2.10.2-Reduction of ketones with Me <sub>2</sub> HSiOTf in the presence of Bu <sub>4</sub> N <sup>+</sup> Y <sup>-</sup> (Y <sup>-</sup> = OTf <sup>-</sup> , Cl <sup>-</sup> , Br <sup>-</sup> ) in chloroform	58
<b>2.11-Reduction of styrene oxide with Me<sub>2</sub>HSiOTf or Me<sub>2</sub>HSiCl in chloroform</b>	59
2.11.1- Reduction with Me <sub>2</sub> HSiOTf in chloroform	59
2.11.2-Reduction with Me <sub>2</sub> HSiCl in chloroform	60
2.11.3-Conclusions	61
<b>2.12-Experimental</b>	63-99
<b>Chapter 3- Introduction to ionic liquids</b>	100-149
<b>3.1-The definition of ionic liquids.</b>	100
<b>3.2-The history of ionic liquids.</b>	100
<b>3.3-Chemical and physical properties.</b>	102
3.3.1-The negligibly small vapour pressure of ionic liquids	102
3.3.2-The conductivity of ionic liquids	102
3.3.3-The polarity of ionic liquids	103
3.3.4-The melting point of ionic liquids	104
3.3.5- The viscosity of ionic liquids	105
3.3.6- The density of ionic liquids	106
3.3.7- Water in ionic liquids and solubility in other media	107

<b>3.4-The synthesis and characterisation of ionic liquids.</b>	109
3.4.1-Preparation	109
3.4.2-The handling and availability of ionic liquids	111
3.4.3-The reaction mechanism of ionic liquid formation	112
3.4.4- Impurities in ionic liquids	112
<b>3.5-Ionic liquids as solvents for catalytic reactions.</b>	114
3.5.1 Hydrogenation reactions	115
3.5.2 Hydroformylation reactions	117
3.5.3-The Heck reactions	121
3.5.4-The hydrodimerisation reaction	125
3.5.5-The Suzuki cross-coupling reaction	127
3.5.6-Oxidation reactions	128
3.5.7-Reduction reactions	129
<b>3.6-Conclusions.</b>	130
<b>3.7-Hydrosilylation: Introduction and literature survey</b>	130
3.7.1- Two types of addition of the silane to the alkene: $\alpha$ and $\beta$ addition	138
3.7.2- Alkene isomerisation	139
3.7.3- Polymerisation of the hydrosiloxane	140
3.7.4- Metal catalysed cleavage of the Si-C bond	141
<b>3.8-Studies of the <math>\alpha</math>:<math>\beta</math> ratio in the hydrosilylation of olefins using different conditions.</b>	141
3.8.1-Hydrosilylation of alkenes	141
3.8.2-Hydrosilylation of alkenyl ethers	145
3.8.3-Hydrosilylation of allylbenzene	146
3.8.4-Hydrosilylation of an $\alpha/\beta$ unsaturated ester	147
3.8.5-Hydrosilylation of but-3-enoic acid	148
3.8.6-Conclusions	149
<b>Chapter 4-Results and Discussion of hydrosilylation of alkenes in Ionic Liquids.</b>	150-186
<b>4.1-Reduction of aldehydes with <math>\text{HSi}(\text{EtO})_3</math> and <math>\text{Me}_2\text{HSiCl}</math> in ionic liquids</b>	151
4.1.1-Reduction of benzaldehyde	151
4.1.2-Reduction of butanal	154
4.1.3-Reduction of octanal	154
4.1.4-Reduction of trimethylacetaldehyde.	155
<b>4.2-Reduction of aldehydes with <math>\text{HSi}(\text{Et})_3</math> in ionic liquids</b>	155
4.2.1-Reduction of benzaldehyde	155
4.2.2-Reduction of butanal	156

4.2.3-Reduction of trimethylacetaldehyde	157
4.2.4 Summary and conclusions	157
<b>4.3-Reaction of silanes in ionic liquids in the absence of aldehydes</b>	158
4.3.1-Hydrolysis/condensation reaction of $\text{MeHSi}(\text{OEt})_2$ in $[\text{BMIM}][\text{OTf}]$ or $[\text{BMIM}][\text{NTf}_2]$	159
4.3.2-Hydrolysis/condensation reactions of $\text{Me}_2\text{Si}(\text{OEt})_2$ in ionic liquids	163
4.3.3-Hydrolysis/condensation reactions of $\text{RSi}(\text{OEt})_3$ where R=methyl, hexyl, phenyl, benzyl in ionic liquids	164
4.3.4- Hydrolysis/condensation reaction of $\text{CH}_3\text{C}_6\text{H}_4\text{Si}(\text{OMe})_3$ and cyclo-pentyl $\text{Si}(\text{OMe})_3$ in ionic liquids	165
4.3.5-Summary of the hydrolysis/condensation reactions of silanes with ionic liquids	166
<b>4.4- Reactions of alkoxydialkylsilanes with aldehydes in the presence of ionic liquids.</b>	167
4.4.1- Reduction of benzaldehyde with $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$ in ionic liquids	167
4.4.2-Reduction of benzaldehyde with $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$ in ionic liquids	168
4.4.3-Reduction of butanal with $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$ or octanal with $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$ in ionic liquids	168
4.4.4-Summary and conclusions	169
<b>4.5-Hydrosilylation of alkenes in ionic liquids</b>	170
4.5.1-Hydrosilylation of alkenes with triethylsilane in ionic liquids using Speier's catalyst	171
4.5.2-Hydrosilylation of alkenes with triethoxysilane in ionic liquids	178
4.5.3-Hydrosilylation of alkenes in the presence of Karstedt catalyst in ionic liquids	180
<b>4.6- Reactions of others nucleophiles in ionic liquids.</b>	181
4.6.1-Bromination of silanes	181
4.6.2-Peterson's reaction	185
<b>Chapter 5-Experimental for ionic liquids investigations</b>	187-216
<b>Further work</b>	217-218
<b>References</b>	219-223
<b>Annex</b>	224-228

## Abbreviations

Acac	acetylacetone
bmim	1-butyl-3-methylimidazolium
Bu <sub>4</sub> N	tetrabutylammonium
C <sub>4</sub> mim	1-butyl-3-methylimidazolium
COD	1,5-Cyclooctadiene
DMCS	dimethylchlorosilane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
emim	1-ethyl-3-methylimidazolium
FTIR	Fourier transform Infra Red
GC	gas chromatography
His	histidine
HMPA	hexamethylphosphoramide
KOR	potassium alkoxide
Li-IM	lithium imidazolid
m	multiplet
Nbd	norbornadiene
NMI	N-methylimidazole
NMR	nuclear magnetic resonance
$\alpha$ -Np	$\alpha$ -naphthyl
M3P	methyl 3-pentenoate
N(Tf) <sub>2</sub>	trifluoromethanesulfonimide
OTf	trifluoromethanesulfonate (triflate)
PMHS	polymethylhydrosilane
TASF	tris(diethylamino)sulfonium difluorotrimethylsilicate
TBAF	tetrabutylammonium fluoride
<sup>t</sup> Bu	<i>tert</i> -butyl
TES	triethoxysilane
TMDS	1,1,3,3-tetramethyldisiloxane
TMS	tetramethylsilane
Triton® B	benzyltrimethylammonium hydroxide
Tf	trifluoromethanesulfonyl
Ts	<i>p</i> -toluenesulfonyl

# Chapter 1

## Chapter 1-Background to organosilicon compounds.

### 1.1. Properties of organosilanes.

Silicon belongs to the fourth group of the periodic table and thus is usually compared with carbon. Comparing silanes to the analogous carbon compounds, we find they are usually more reactive, particularly to nucleophilic substitution, because of their larger size, lower electronegativity and the availability of low-energy d orbitals. Silicon does not possess the multitude of bonding configurations of carbon but as a semi-metal it has a tendency to form stable tetravalent compounds and form bonds with most of the other elements of the periodic table. Silicon thus has a rich inorganic, organic and organometallic chemistry.

Silicon compounds are often polarised in the opposite sense to carbon compounds since the positive charge is localised on the silicon, leading to bond polarisation in the sense:  $\text{Si}^{\delta+}-\text{H}^{\delta-}$ . This means that the silicon can be easily attacked by nucleophiles and gives the hydrogen in the silicon-hydrogen bond a hydridic character. Substitution at silicon happens more readily with much poorer leaving groups than does substitution at carbon. This tendency to nucleophilic attack means that the halosilane can be used as the starting material for the formation of many compounds, in particular silicon-oxygen bond formation to form organosiloxanes.

A comparison of Si-X and C-X bond strengths clearly shows the difference between the two elements. The bonds between oxygen or halogen and silicon are very strong and Si-F is one of the strongest single bonds between any two elements in the periodic table. In contrast, the bonds between N, Si and H are much weaker. The different values are presented in the following Table, which shows the bond dissociation energies as well as the bond lengths.

Bond	Compound	D (kJ/mol <sup>-1</sup> )	r (Å)	Bond	D (kJ/mol <sup>-1</sup> )	r (Å)
Si-Si	H <sub>3</sub> SiSiH <sub>3</sub>	308	2.34	C-C	334	1.53
Si-H	Cl <sub>3</sub> SiH	378	1.48	C-H	420	1.09
	H <sub>4</sub> Si	382	-			
Si-O	Me <sub>3</sub> Si-OH	536	1.63	C-O	340	1.41
	Me <sub>3</sub> Si-OSiMe <sub>3</sub>	549	-			
Si-N	(Me <sub>3</sub> Si) <sub>2</sub> NH	320	1.74	C-N	335	1.47
Si-F	Me <sub>3</sub> SiF	665	1.6	C-F	452	1.39
Si-Cl	Me <sub>3</sub> SiCl	472	2.05	C-Cl	335	1.78
Si-Br	Me <sub>3</sub> SiBr	402	2.21	C-Br	268	1.94
Si-I	Me <sub>3</sub> SiI	321	2.44	C-I	213	2.14
Si-C	H <sub>3</sub> SiMe	369	1.87	C-C	334	1.53

**Table 1: Table of bond dissociation energies (D) and bond lengths (r) for Si-X and C-X compounds<sup>1</sup>.**

In spite of the very strong Si-F bond molecules containing these bonds are kinetically very reactive. Thus F<sup>-</sup> can be used as a catalyst for the cleavage of other Si-X bonds. The values in Table 1 apply to tetracoordinate species; with five or six-co-ordinate specie; there is a corresponding increase in bond lengths<sup>2</sup>.

It has been suggested that stronger bonds are formed with more electronegative groups because of the increase in contribution from ionic structures of the type Si<sup>δ+</sup>-X<sup>δ-</sup><sup>3</sup>. A comparison of the ionic character of bonds involving silicon and carbon with other atoms in poly-dimethylsiloxanes is presented in Table 2<sup>4</sup>:

Element X	Ionic character (in %) for Si-X bond	Ionic character (in %) for C-X bond
Si	-	12
C	12	-
H	2	4
O	50	22

**Table 2: Ionic character (in %) of Si-X and C-X bonds (X = Si, C, H and O)**

The values in Table 2 show a high ionic character for the silicon-oxygen bond compared to the carbon-oxygen bond: this separation of charge also explains the higher susceptibility of the silicon to nucleophilic attack.

## **1.2-Nomenclature of organosilicon compounds.**

### **1.2.1-Nomenclature of organosilanes.**

As with carbon, silicon nomenclature is based on the simplest hydrosilane,  $\text{SiH}_4$ , where one or more hydrogen atoms can be exchanged for an alkyl or halogen function. As with organic compounds, alphabetical order takes precedence. For example,  $\text{Me}_2\text{SiCl}_2$  is named dichlorodimethylsilane,  $\text{H}_3\text{SiSiH}_3$  disilane,  $\text{Ph}_3\text{SiSiMe}_3$  is named 1,1,1-trimethyl-2,2,2-triphenyldisilane and  $\text{Me}_2(\text{Ph})\text{SiCl}$  will be written as chlorodimethylphenylsilane.

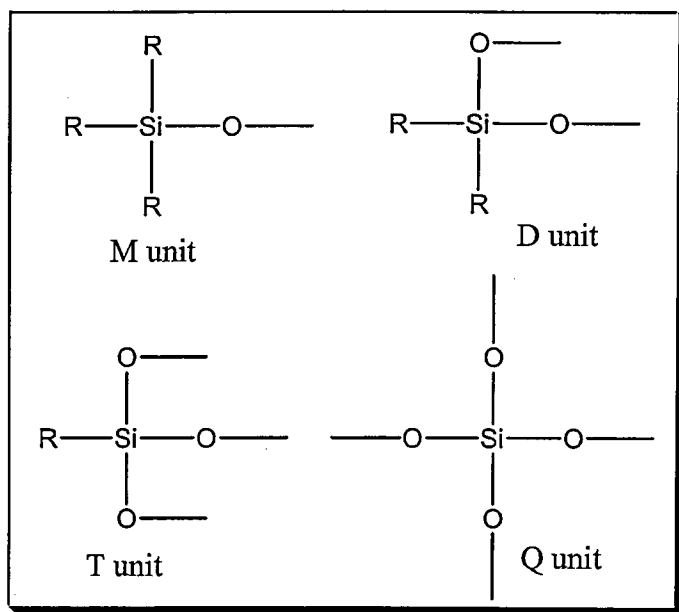
### **1.2.2 Nomenclature of organosiloxanes.**

Silicon compounds containing silicon-oxygen bonds are known as organosiloxanes. Polysiloxanes are silicon polymers and the name of the polymer depends upon how many silicons are present in the polymer and how many oxygens are attached to each silicon. If the silicon is attached to one oxygen it is a monofunctional unit, M, with two oxygens it is a difunctional unit, D, three oxygens lead to a trifunctional unit, T, and four oxygen lead to



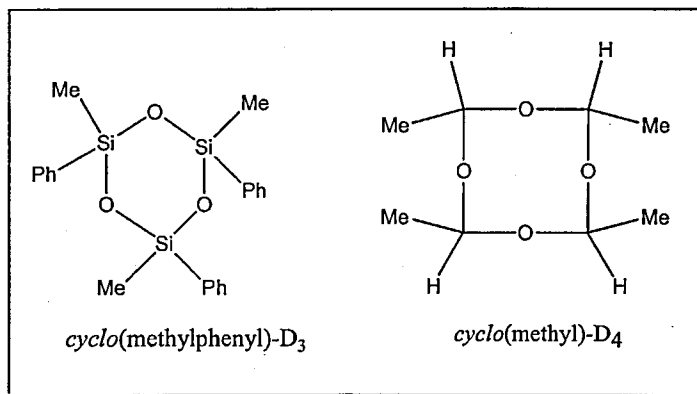
quadrifunctional unit, Q. Following the type of unit is a number which represents the number of silicon atoms present in the polymer, written as a subscript. For example,  $\text{H}_2(\text{RO})\text{Si}[\text{OSiH}_2]_2\text{OSi}(\text{OR})\text{H}_2$  is a  $\text{D}_4$  linear tetramer.

The different units are represented in Figure 1:



**Figure 1: M, D, T and Q units for polysiloxanes.**

With complex siloxanes, the name starts with the name of the R groups present on the silicon, then the unit and then the subscript. Cyclic systems are named in the same way as linear ones but with the prefix *cyclo*.



**Figure 2: Examples of *cyclo*-polysiloxanes.**

### 1.3-Analytical and spectroscopic techniques for silicon compounds.

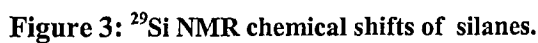
#### 1.3.1- $^{29}\text{Si}$ NMR spectroscopy.

$^{29}\text{Si}$  NMR spectroscopy is widely used as an analytical technique for the analysis of silicon containing compounds. This method is simple, efficient and non-destructive of the silicon compound.

The  $^{29}\text{Si}$  isotope has a spin quantum number  $I = 1/2$  and a low abundance of only 4.7 %. This low abundance and a long relaxation time were two of the initial problems in the application of this analytical technique, until the introduction of Fourier-Transform-NMR spectroscopy (FT-NMR).

The chemical shift range for compounds containing silicon is large, spanning some 200 ppm. This shift is dependent on the geometry of the silicon (coordination number) and the different substituents on the silicon atom. For example, the chemical shift increases when  $\text{SiH}_4$  is replaced by methyl groups and then decreases as the methyl groups are replaced by electronegative groups such as chlorine. An increase in the chemical shift is also observed with a co-

3 and  $4^5$ .





in the presence of nucleophiles or salts. The following is a brief review of such a reduction, involving an intermediate hypercoordinated silicon, which activates the Si-H bond.

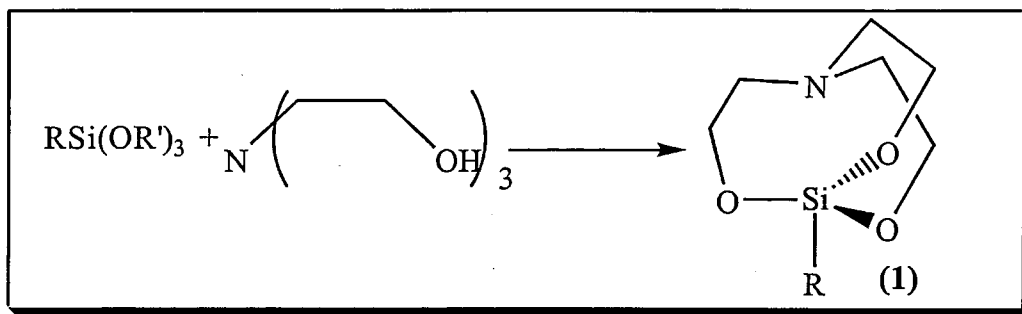
Pentacoordinate silicon species can be prepared using three different methods:

- 1) by addition of a bidentate or multidentate ligand (charged or neutral) to an organosilane.
- 2) by inter- or intra-molecular coordination of a neutral donor to silicon, giving a neutral complex.
- 3) by addition of an anion to an organosilane or to a spirosilane to give an anionic pentacoordinate silicon complex.

Examples of these methods are discussed in more detail below, together with the reactivity of the pentacoordinate silicon compounds that are formed in the reduction of carbonyl compounds.

#### 1.4.1-Formation by substitution of a trifunctional organosilane.

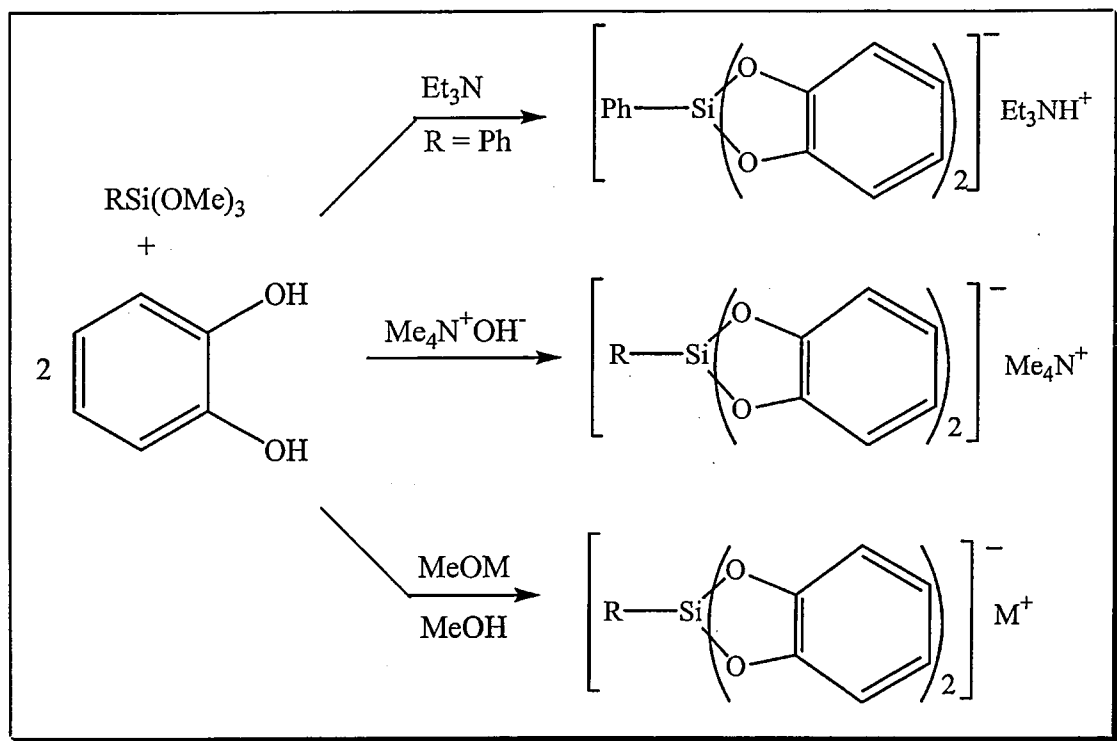
Frye and co-worker<sup>8</sup> were the first to report the reaction of triethylamine derivatives with trifunctional silanes to give a pentacoordinate structure (**1**), as shown in Scheme 1.



**Scheme 1: Preparation of silatranes.**

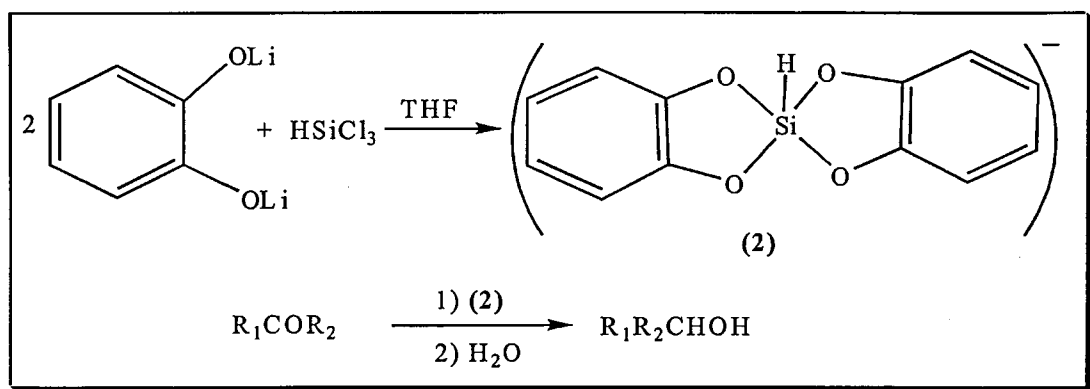
An early report by Eaborn<sup>9</sup> suggested that neutral pentacoordinate silicon hydrides, such as silatrane (1) with R = H, have potential as reducing agents for some organic compounds, including halides, azoxybenzene and carbonyl compounds. In the last case effective addition of hydride to the carbonyl bond occurs, the alcohol being formed upon subsequent hydrolysis. However, the yields of the reactions are often low; for example, with *p*-HOC<sub>6</sub>H<sub>4</sub>CHO the yield is 32 % after 72 h in refluxing xylene.

Catechol and its derivatives can react with trialkoxysilanes in the presence of a base, to give anionic pentacoordinate silicon species. (Scheme 2).



**Scheme 2: Catechol silanes.**

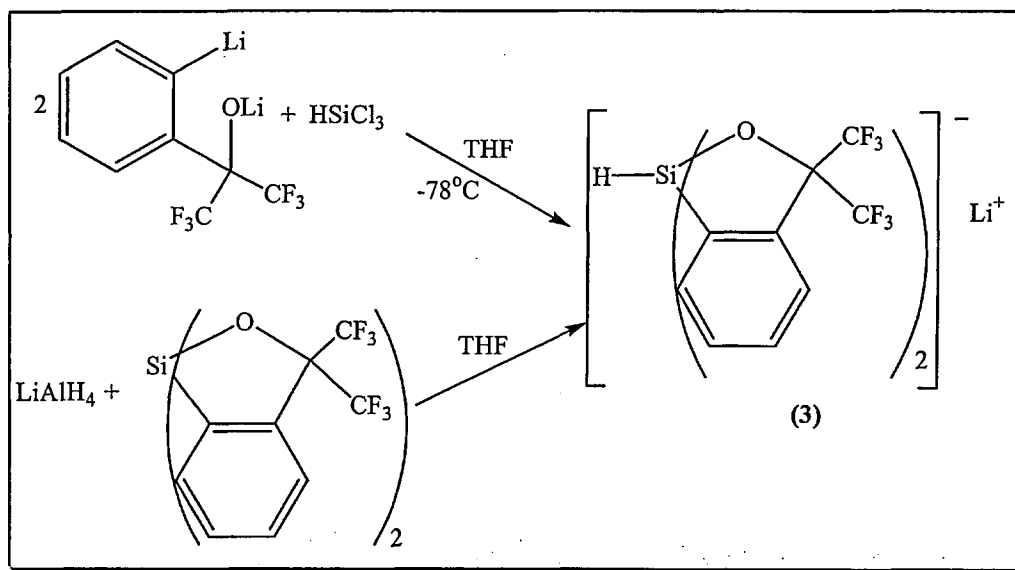
Hata and co-workers<sup>10,11</sup> found the pentacoordinated species **(2)**, derived from trichlorosilane and catechols or 2,2'-dihydroxybiphenyl in THF, could reduce aldehydes and ketones without any catalyst in high yield (Scheme 3).



**Scheme 3: Synthesis and reactivity of hydrido-bis(catechol)silanes.**

Characterisation and isolation of **(2)** failed, although its formation was confirmed by the reduction of aldehydes and ketones without a catalyst.

The only such pentacoordinate species that has been isolated up until now resulted either from the reaction between trichlorosilane and the dilithio derivative of the hexafluorocumyl alcohol or from the reaction of the spirosilane (3) with lithium aluminium hydride<sup>12, 13</sup> (Scheme 4).



**Scheme 4: Formation of pentacoordinate species via two routes.**

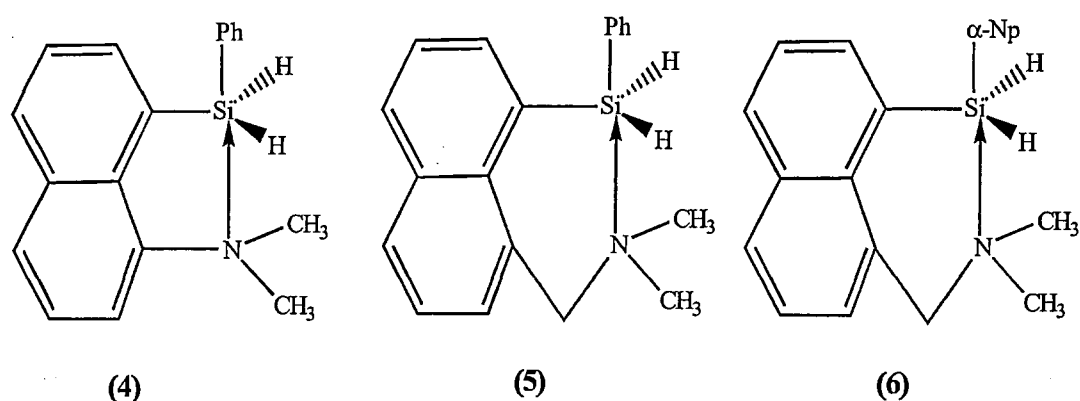
However, no general synthetic route has been developed for the formation of pentacoordinate anionic hydridosilicates. The *in situ* generated species (2) and the reagent (3) have both been found to be effective reducing agents towards aldehydes and ketones.



#### 1.4.2-Neutral donation to an organosilane

- Using intramolecular donation

An alternative way of obtaining pentacoordinate silicon species is by intramolecular donation to an organosilane. Corriu *et al*<sup>14, 15</sup> have used this method to obtain the pentacoordinate silicon species (4), (5) and (6), as shown in Figure 5.



**Figure 5: Formation of pentacoordinate silicon species by Corriu.**

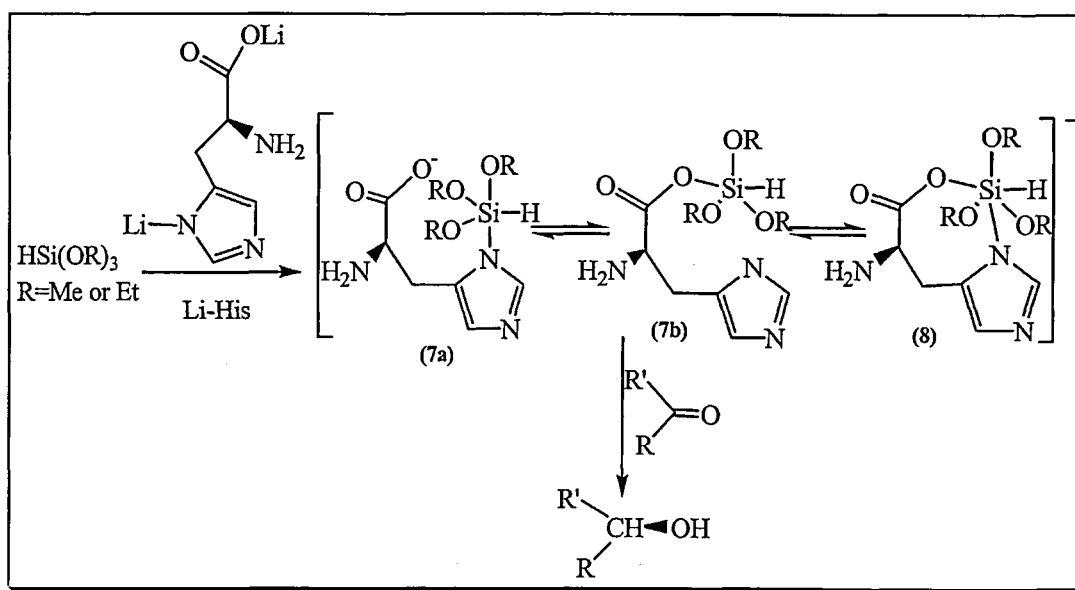
The rigid geometry of these structures facilitates intramolecular extracoordination from the donor group<sup>16</sup>.

Corriu has examined the reactivity of such pentacoordinate silicon dihydrides<sup>17</sup>, with alcohols, carboxylic acids and carbonyl compounds. The dihydride is remarkably more reactive, in the reduction of aldehydes and ketones, than the corresponding tetracoordinate species<sup>18, 19</sup>.

- Using (EtO)<sub>3</sub>SiH and N-Methylimidazole.

Imidazole and its derivatives activate silicon by nucleophilic attack with remarkable efficiency, and are used as catalysts in the preparation of silyl ethers from alcohols. Bassindale *et al*<sup>20</sup> established the pentacoordinate nature of the interaction between N-methylimidazole (NMI) and chlorodimethylsilane (DMCS) using <sup>29</sup>Si NMR spectroscopy.

LaRonde and Brook<sup>21</sup> were interested in examining how imidazole could be used to facilitate the extracoordination of hydrosilanes to give pentacoordinate compounds that reduce carbonyl groups. They studied the reduction arising from catalytic amounts of NMI, lithium imidazolides (Li-IM) and mono- or di-lithium salts of histidine (Li-His and Li<sub>2</sub>-His). Imidazole and histidine did not catalyse the reaction between triethoxysilane and acetophenone and only starting materials were recovered. The reduction of ketones took place at 0 °C over 24 hours when catalysed by imidazolidine and histidyl anions, *via* the pentacoordinate species shown in Scheme 5.

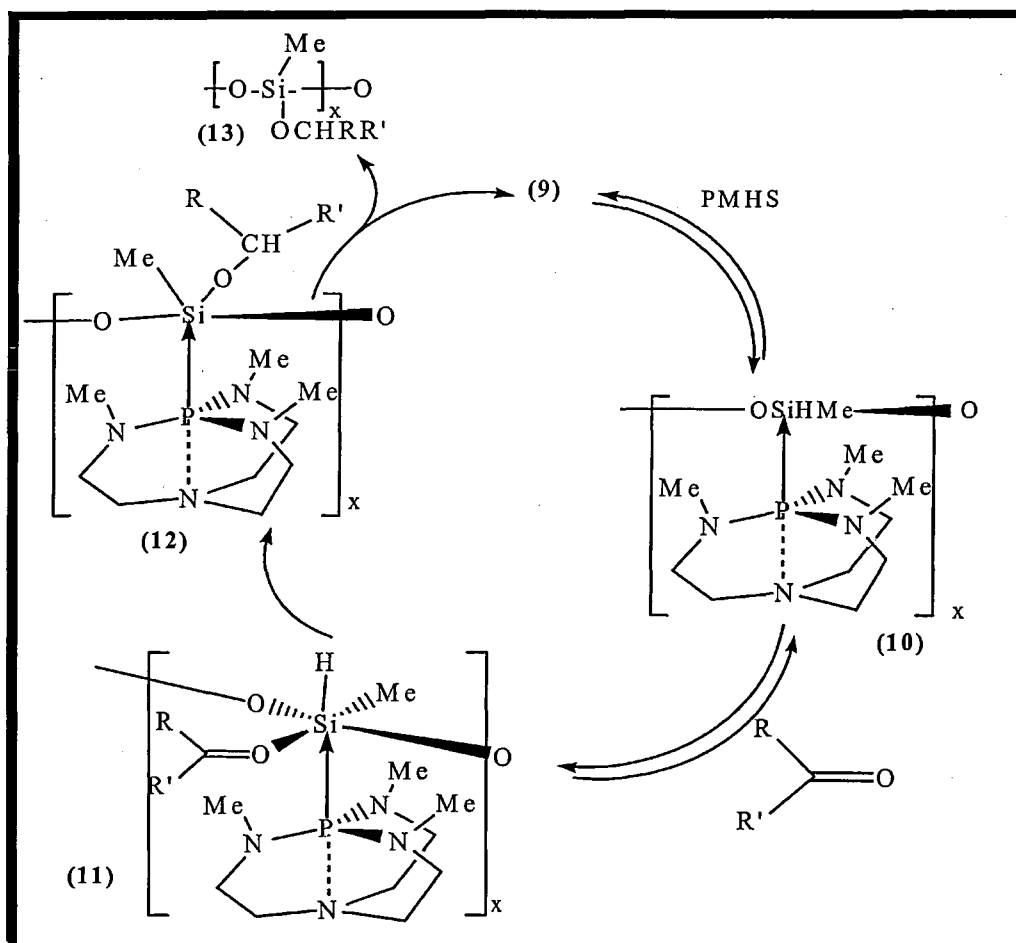


**Scheme 5:** *In situ* preparation of extracoordinate hydrosilanes in THF solution and their reactivity towards prochiral ketones.

Imidazole is commonly used to activate silicon to nucleophilic attack when good leaving groups such as chloride are involved. With a poorer leaving group, such as hydride, more powerful silanucleophiles are required, such as imidazolide or the histidyl dianion. Since the mono- and di-anion of histidine reduce acetophenone with the same enantioselectivity, this suggests that either the monodentate structure (7a) and (7b) or bidentate structures (8) are involved in both cases.

- Using  $P((Me)NCH_2CH_2)_3N$  and polymethylhydrosilane (PMHS) as silane.

In 1973, Lipowitz was the first to report the reduction of aldehydes and ketones by PMHS,  $-(O-SiMeH)_n-$ , in the presence of bis(dibutylacetoxytin)<sup>22</sup>. Recently, Wang, Wroblewski and Verkade<sup>23</sup> found another efficient promoter for the reduction of aldehydes and ketones with PMHS, namely  $P(MeNCH_2CH_2)_3N$  (9), which co-ordinated with PMHS to give a pentacoordinate silicon (10). Aliphatic aldehydes are reduced to the corresponding alcohols in high yields and aromatic ketones are also efficiently reduced. The mechanism of this reaction is shown in Scheme 6: the phosphorus atom in (9) initially co-ordinates with the silicon atom to form the corresponding pentacoordinate hydrosilicate (10). The pentacoordinate silicate then co-ordinates with the oxygen of a carbonyl compound to give a hexacoordinate hydrosilicate (11). This is followed by a hydride transfer to the carbon of the carbonyl compound (12). The reaction is completed by the formation of the silyl ether linkage (13).



**Scheme 6: Mechanism for the reduction of carbonyl compounds**

• Using  $\text{Cl}_3\text{SiH}$  and dimethylformamide (DMF).

Trichlorosilane-dimethylformamide was found to be a good reducing agent for the reduction of aldehydes to alcohols, imines to amines and also the reductive amination of aldehydes<sup>24</sup>. The reduction of aldehydes proceeded smoothly without any catalyst ( $\text{F}^-$ , etc) at  $0^\circ\text{C}$  for four to six hours using trichlorosilane in DMF-dichloromethane to give the corresponding alcohols in high yields (85-98 %). No reaction occurred in dichloromethane, acetonitrile, benzene, or tetrahydrofuran even at room temperature without DMF. Highly chemoselective reduction of aldehydes was achieved in the presence of an aryl chloride, aryl

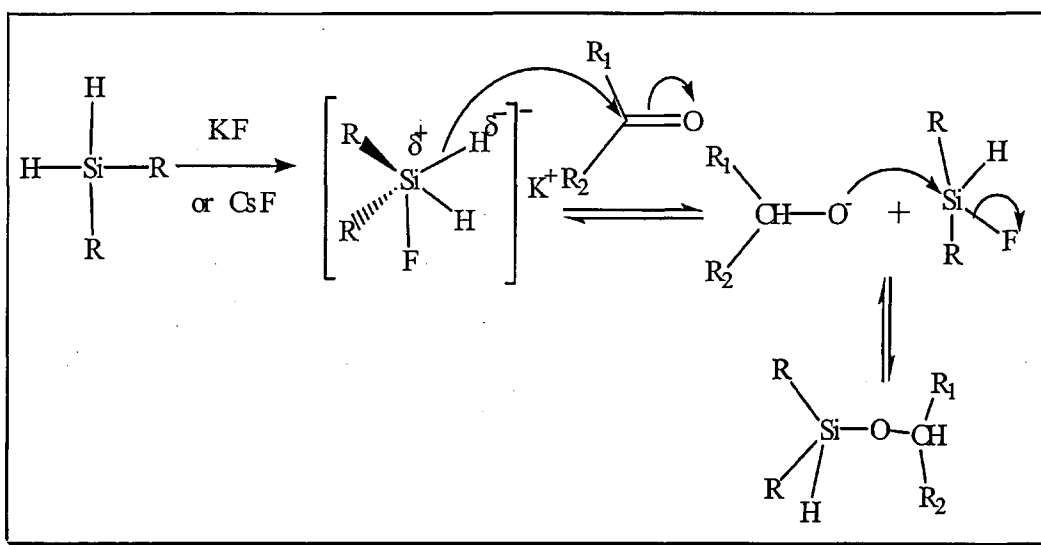
nitro group and double or triple bonds. For the reduction of ketones, a longer reaction time was required, and the secondary alcohols were obtained in good to high yields. Reduction of an aldehyde rather than a ketone was performed with more than 98 % selectivity<sup>25</sup>.

#### 1.4.3-Co-ordination of anions to tetracoordinate silicon compounds.

This mechanism of reduction involves the formation of a pentacoordinate silicon, which reacts, *via* hexacoordination, with the carbonyl group. An improvement in the yield of the reduction reaction could be achieved by using a pentacoordinate silicon such as five coordinate potassium dihydrosilicate.

- Using KF or CsF as anions and (RO)<sub>3</sub>SiH as the silane.

Corriu has reported a simple method for the reduction of carbonyl compounds, involving potassium or cesium fluoride-induced hydrosilylation in the absence of a solvent<sup>26, 27</sup>. It is possible that the role of the salt is to activate the silicon atom by anionic co-ordination to give the pentacoordinate silicon in which the Si-H bond is weakened (Scheme 7).



**Scheme 7: General formation of pentacoordinate silicon *via* fluoride ion donation and its reactivity towards carbonyl groups.**

This method is very selective and carbonyl compounds are reduced in the order aldehydes > ketones > esters in the presence of KF or CsF. The salt promotes the hydrosilylation of aldehydes below 20 °C (using KF), ketones between 30 and 60 °C and esters between 80-100 °C (requiring the use of CsF). The efficiency of the salts increases when the cation-anion interaction decreases in the order  $\text{LiF} \ll \text{KF} < \text{CsF}$ . Therefore, it is possible to reduce aldehydes in the presence of ketones and ketones in the presence of carboxylic esters by controlling the temperature or the nature of the salt.

The Si-H bond, activated by KF or CsF, is a very powerful and selective reducing agent and the carbonyl group can be reduced without reduction of other functional groups; for example, conjugated C=C and isolated C-C were not affected, and imides and nitriles did not react. The conversion of amides and acid chlorides to alcohols was very slow, whilst nitro and bromo groups remain

unchanged. This allows selective reduction in the case of bifunctional compounds.

Owing to the high cost of the dihydrosilane used ( $\text{Ph}_2\text{SiH}_2$  or phenyl  $\alpha$ -naphthylsilane), this method does not compare well with other synthetic methods such as catalytic hydrogenation or reduction using metallic hydrides.

An improved procedure for the selective reduction of carbonyls has been developed where the rate of the hydrosilylation is greatly affected by the use of solvents and the nature of the silane<sup>28</sup>. The nature of the silane affects the rate of the reduction in the order  $\text{HSiR}_3$  (R = alkyl group) <  $(\text{EtO})\text{SiR}_2\text{H}$  <  $(\text{EtO})_2\text{SiRH}$  <  $(\text{EtO})_3\text{SiH}$ , thus hydrosilanes become more reactive on increasing their electrophilicity by the inclusion of an electron-withdrawing group on the silicon atom. The use of hydrosilanes in DMF and DMSO gives the best results since the use of these solvents has two major advantages over the previous methods:

- 1) carboxylic acids and esters can be reduced in the presence of potassium fluoride instead of the more expensive caesium fluoride.
- 2) The silanes  $\text{HSiMe}(\text{OEt})_2$  and PMHS, although less reactive than  $(\text{EtO})_3\text{SiH}$ , are more reactive in these solvents making the isolation of the alcohols more straightforward.

- Using TBAF as the anion

Due to the low solubility of KF in the solvents used, it is assumed that the hydrosilylation reactions using this reagent proceed through heterogeneous catalysis.

Fujita and Hiyama<sup>29-31</sup> have developed a convenient method, using hydrosilanes in the presence of catalytic quantities of tetrabutylammonium fluoride (TBAF) or tris(diethylamino)sulfonium difluorotrimethylsilicate (TASF) as the fluoride ion sources, in the polar aprotic solvent HMPA. In contrast to Corriu's salt-promoted reaction, it was found that since TBAF or TASF are soluble in polar aprotic solvents the reaction is homogeneous. The use of HMPA markedly accelerated the reaction (reaction complete within one hour) and the aldehydes and ketones could be reduced at room temperature. Also TBAF is easy to handle, cheap and commercially available.

- Using KOR as the anion.

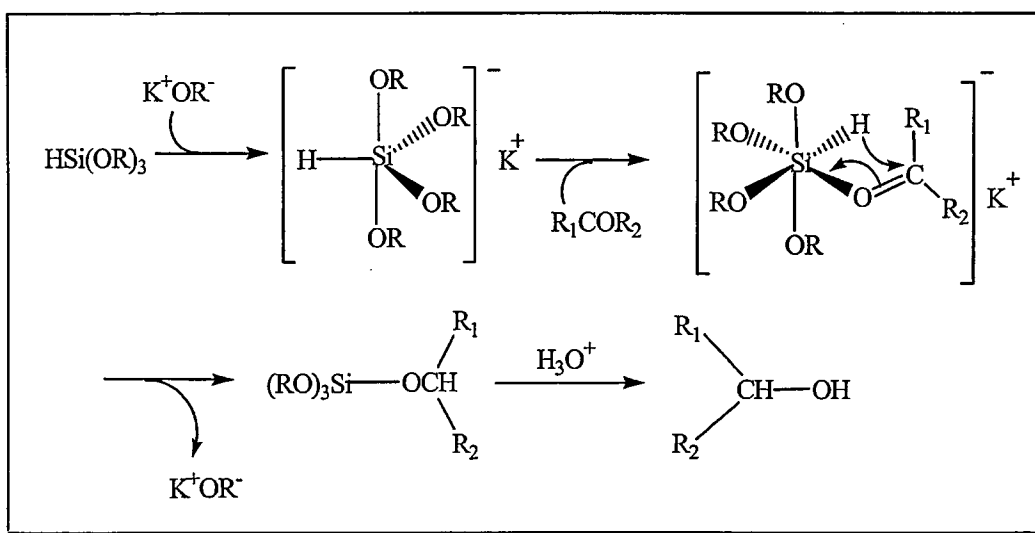
Becker and Henner<sup>32</sup> obtained  $K^+[H_2Si(OR)_3]^-$  by reacting  $(RO)_3SiH$  with potassium hydride. The isolated  $K^+[H_2Si(OR)_3]^-$  ( $R = ^iPr$ ) was found to reduce carbonyl compounds in the absence of a catalyst under mild condition and the yields of primary and secondary alcohols are generally high (50-80%). The lower yield in the case of  $PhCOCH_3$  can be attributed to a partial enolisation of the ketone by the alkoxide ions liberated during the reaction. They found that, like fluoride and alkoxide, hydride co-ordinated with silicon to give potassium



dihydrosilicates as the intermediate, which show a high reactivity as a reducing agent for carbonyl compounds.

Other anionic hydridosilicates have been prepared by Guerin *et al*<sup>32-34</sup>, by coordination of KOR to  $\text{HSi(OR)}_3$  ( $\text{R} = \text{Et}, ^i\text{Pr}, \text{Ph}$ ) in THF without the addition of 18-crown-6. This reagent was able to reduce carbonyl groups without further activation. This demonstrates the high reactivity of the Si-H bond in compounds of the type  $[\text{HSi(OR)}_4]^-$ , which also readily undergoes a one electron transfer to an appropriate substrate. The reaction occurs quickly at room temperature in THF and the yields of primary and secondary alcohols were generally excellent (up to 90 %).

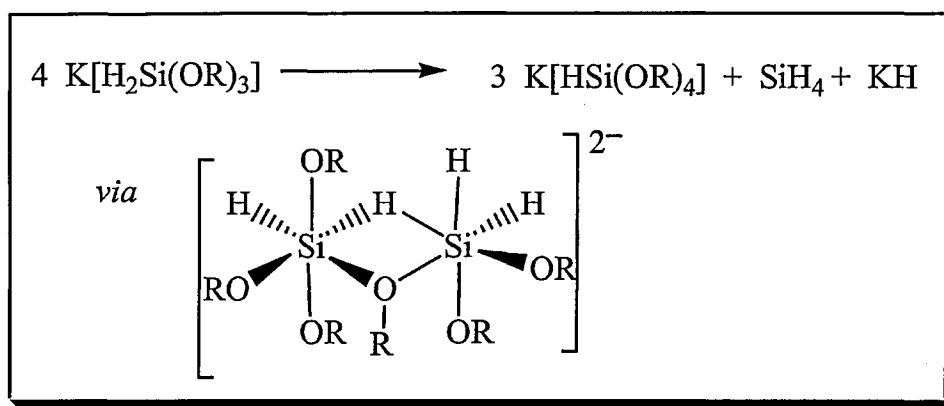
The reduction of benzophenone gave only benzhydrol, with no trace of the blue ketyl radical anion during the reaction, and thus no benzopinacol was recovered. This is indicative of a polar mechanism, such as that shown in Scheme 8.



**Scheme 8: Formation of pentacoordinate silicon *via* alkoxide donation and reaction with carbonyl compounds.**

In 1997 Kagan described the asymmetric catalytic reduction of ketones with hypervalent trialkoxysilanes<sup>35</sup> due to the activation of the silane with a small amount of a chiral nucleophile. The nucleophile added to the silane and then underwent addition to the ketone, which gave, after aqueous work up, the corresponding alcohol.

Recently, Corriu *et al*<sup>33,36</sup> have shown that  $\text{K}[\text{H}_2\text{Si}(\text{OR})_3]$  ( $\text{R} = \text{Me, Et, } ^n\text{Bu}$ ) undergoes a redistribution reaction, as shown in Scheme 9.



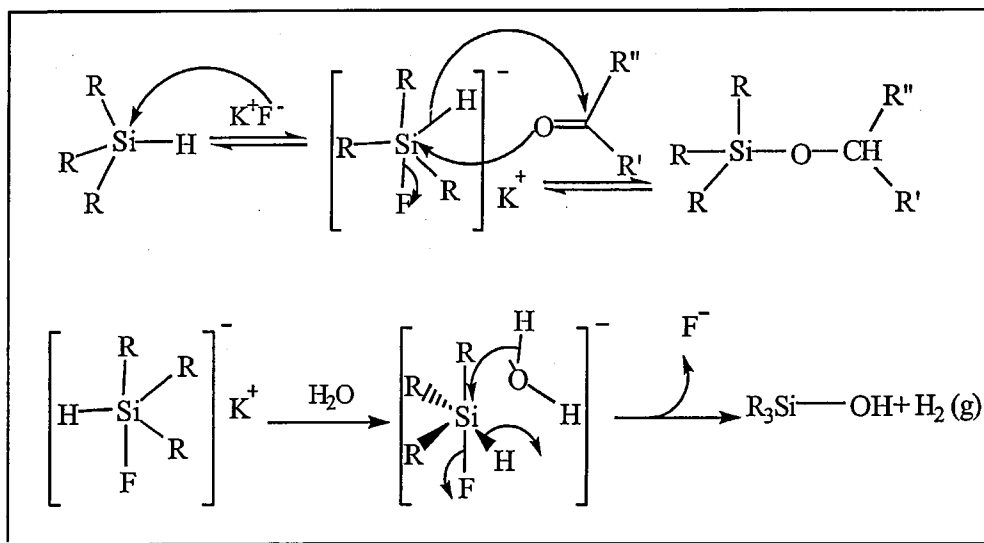
**Scheme 9:** Redistribution of  $\text{K}[\text{H}_2\text{Si}(\text{OR})_3]$  ( $\text{R} = \text{Me, Et, } n\text{-Bu}$ ).

An increase in the basicity of the solvent, on going to DME from THF, was found to accelerate the formation of  $\text{K}[\text{HSi}(\text{OR})_4]$ . In contrast, the presence of 18-crown-6 seems to stabilise greatly the dihydrosilicate anionic species<sup>37</sup>.

- Using KF as anion and  $\text{R}_3\text{SiH}$  as silane

Nucleophilic assistance of the reactions of silicon-hydrogen bonds has been studied by Reye, Perz and Boyer<sup>33</sup>. They used different hydrosilanes such as  $\text{R}_3\text{SiH}$ , with  $\text{R} = \text{Ph, Me, } \alpha\text{-Np}$ , and reacted them with KF salt. The mechanism they proposed involves the co-ordination of  $\text{F}^-$  at silicon, followed by a

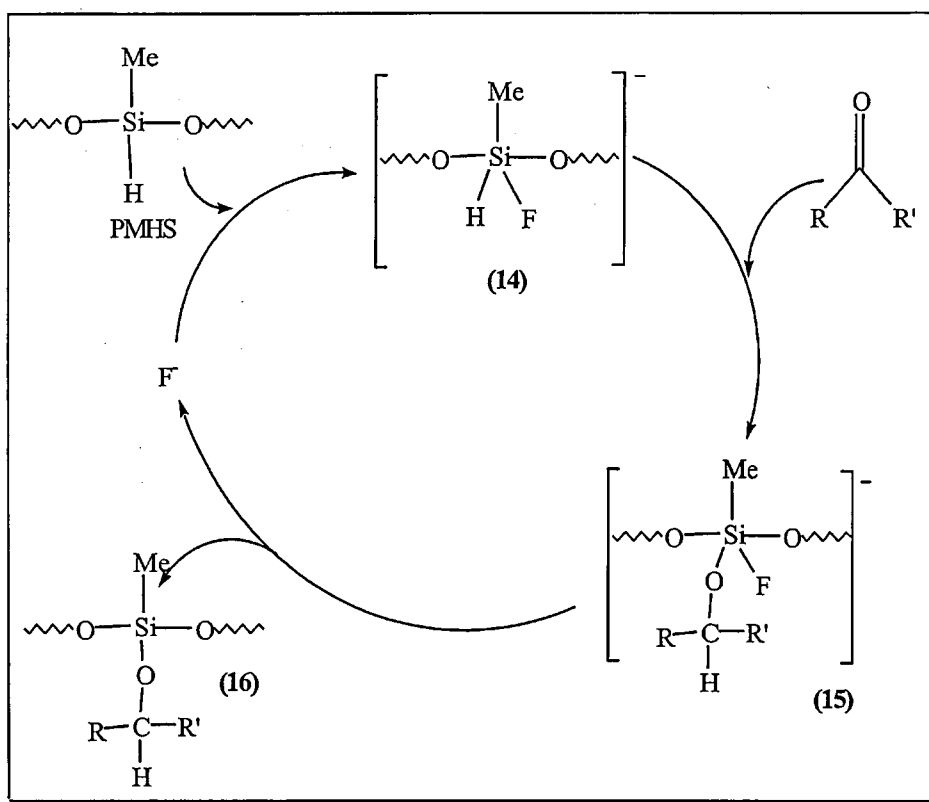
concerted attack of the oxygen of the carbonyl group at silicon with formation of an alkoxyasilane after the transfer of hydride to the electrophilic carbon<sup>38</sup>.



**Scheme 10: Reaction of  $[\text{R}_3\text{Si(F)H}]^-$  with water: the intermediate is moisture sensitive.**

- Using TBAF as anion and PMHS as solvent

Among the organosilanes studied thus far, polymethylhydrosiloxane (PMHS) is an attractive reagent for the reduction of carbonyl compounds because of its low price, stability against air and moisture and easy handling. Reduction of aldehydes and ketones with PMHS proceeded smoothly in the presence of  $\text{Bu}_4\text{NF}$  at  $-70\text{ }^\circ\text{C}$  or  $0\text{ }^\circ\text{C}$  within 60 min in THF<sup>35</sup>. Based on the mechanism for the reduction of carbonyl compounds with hydrosilanes catalysed by fluoride anion<sup>39, 40</sup> the PMHS reduction seems to follow the cycle illustrated in Scheme 11.



**Scheme 11: Cycle of reduction of carbonyl compounds with hydrosilanes catalysed by fluoride anion.**

Fluoride anion in THF attacks the silicon atom of PMHS to generate the reactive pentacoordinate hydrosilicate **(14)** or the THF-co-ordinated hexavalent silicates, which deliver the hydride to the carbonyl carbon to afford the intermediate **(15)**. Production of fluoride anion and the silyl ether **(16)** then completes the cycle. The steric interaction between the carbonyl compound and the bulky polymeric species **(14)** are apparently responsible for the observed high stereoselectivity. Non-volatile polar aprotic solvents such as HMPA, DMF and DMSO are not necessary and thus THF was a good solvent for the reduction.

Additionally, Triton<sup>®</sup> B (benzyltrimethylammonium hydroxide), a catalyst that is considerably cheaper than TBAF, is an excellent promoter of the reduction

process<sup>41</sup>. These homogeneous reactions exhibit the same chemoselectivity as the heterogeneous reactions described by Corriu and co-workers; in particular nitro, bromo, chloro, cyano and fluoro groups are tolerated. In addition the system tolerates alkene functionalities.

### **1.5-Conclusions.**

Since silicon atoms possess vacant d orbitals they can expand their coordination. This increase in coordination number can be achieved using bidentate ligands, neutral donors, or salts. Tetracoordinate silicon atoms are usually positively polarised due to the low electronegativity of the silicon and adding an electronegative ligand leads to a more electropositive silicon atom that will be more receptive to nucleophilic attack. Thus carbonyl compounds can be reduced using silanes, where the silicon-hydrogen bond is activated by extra-co-ordination leading to the conversion of aldehydes into alcohols. Based on examples from the literature, the next chapter will focus on the reduction of carbonyl compounds by hydrosilanes using different types of nucleophile, based on their ability to co-ordinate to the silicon atom.

# Chapter 2

## **Chapter 2- Reductions of carbonyl compounds by hydrosilanes activated by nucleophiles**

Organosilicon compounds are increasingly in demand and many reactions such as reductions involve the use of silicon compounds as reagents. As discussed in chapter 1, hydrogen-containing silanes have been shown to be good reducing agents in the presence of catalysts, which control the reactivity and selectivity of the reduction reaction.

This study examines the hydrosilylation of unsaturated organic compounds such as aldehydes and ketones, by an Si-H reducing agent and in particular  $\text{Me}_2\text{HSiX}$  where X = trifluoromethanesulfonate (OTf), chloride (Cl), bromide (Br) or iodide (I).

The reaction was studied using different conditions; for example, in the presence or absence of salts, nucleophiles and amberlyst polymers.

NMR spectroscopy is sensitive enough to follow the reduction reactions of unsaturated organic compounds with Si-H containing species. The reduction was monitored using  $^1\text{H}$ ,  $^{13}\text{C}$  and sometimes  $^{29}\text{Si}$  NMR spectroscopy, while silicon- $^{29}$  NMR was able to provide information about the co-ordination number of the silicon species in these reactions. GC provided a quantitative

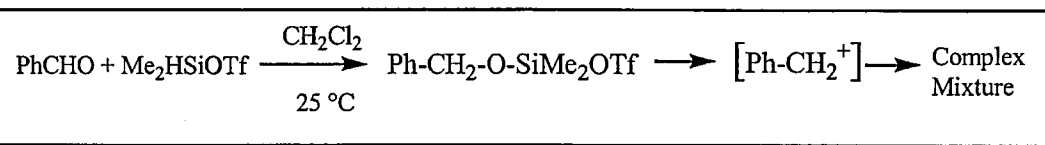
analysis, which allowed calculation of the yields of the reactions using xylene as an internal standard.

## 2.1-Reduction of aldehydes with Me<sub>2</sub>HSiOTf in chloroform.

The reduction of aldehydes *via* hydrosilylation usually requires a catalyst. This is because most silanes are relatively inert. In this study we used the silane Me<sub>2</sub>HSiOTf, which contains a good leaving group, triflate, such that the silane had an enhanced reactivity towards reduction.

### 2.1.1-Reduction of benzaldehyde.

The reaction of benzaldehyde with dimethylsilyltriflate in chloroform is an exothermic and violent reaction at room temperature. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products show a range of peaks suggesting a complex mixture with numerous products. The <sup>13</sup>C NMR spectra contain CH<sub>2</sub> signals in the region of 30-40 ppm arising from the reduction of the benzaldehyde to a methylene group. Equation 1 describes this reduction.



Equation 1

Nevertheless, a signal at 201.1 ppm in the <sup>13</sup>C NMR spectrum of the reaction mixture shows the presence of some starting material that did not react. In order to control the reaction, the reaction was run at 0 °C. The <sup>13</sup>C NMR spectrum of the product still contains signals between 30-40 ppm although they were much



smaller. A new compound was formed during the reaction corresponding to dibenzyl ether, in 21 % isolated yield. Again the benzaldehyde is not totally reduced, giving a  $^{13}\text{C}$  NMR signal at 201.1 ppm.

#### 2.1.2-Reduction of octanal, $\text{CH}_3-(\text{CH}_2)_6-\text{CHO}$

As with benzaldehyde, the reaction was performed using  $\text{Me}_2\text{HSiOTf}$  in chloroform at 0 °C. The reaction leads to the reduction of the octanal giving mainly dioctyl ether in 27 % isolated yield. Confirmation that the carbonyl group is reduced to  $\text{CH}_2$  is given by the  $^{13}\text{C}$  NMR, which shows the signal at 202.7 ppm disappearing and a new signal at 71.8 ppm appearing.

#### 2.1.3-Reduction of trimethylacetaldehyde

The reaction of  $\text{Me}_3\text{CCHO}$  with  $\text{Me}_2\text{HSiOTf}$  is exothermic. After hydrolysis with water, the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra showed that the reaction at 0 °C had resulted in the formation of bis-(2,2-dimethylpropyl) ether, 2-methylpropan-2-ol and dimethylsiloxanes. The yield of this reaction is poor (about 10 % of the ether).

#### 2.1.4-Reduction of 2-methylbutanal.

2-Methylbutanal was also reacted with  $\text{Me}_2\text{HSiOTf}$  in chloroform at 0 °C to give the corresponding dialkyl ether and alcohol. The yield of the reduced products is 16 % of the ether and less than 10 % for the alcohol.

### 2.1.5-Mechanism of reduction of aldehydes by $\text{Me}_2\text{HSiOTf}$ .

The first step should be the formation of a pentacoordinate silicon arising from the attack at the silicon by the oxygen of the aldehyde. The hydrogen in this pentacoordinate species is hydridic because of the polarisation  $\text{Si}^{\delta+}-\text{H}^{\delta-}$ . Thus, it can migrate to the electrophilic carbon attached to the oxygen. The result is the formation of an intermediate species,  $\text{RCH}_2\text{-O-Si(CH}_3)_2\text{OTf}$ , which then reacts further to give the alcohol and ether.

Subsequent experiments suggested that careful work up is required to optimise the yield of such products.

The pentacoordinate silicon species might be expected to readily lose triflate to revert to a tetracoordinate silicon in preference to transferring hydrogen.

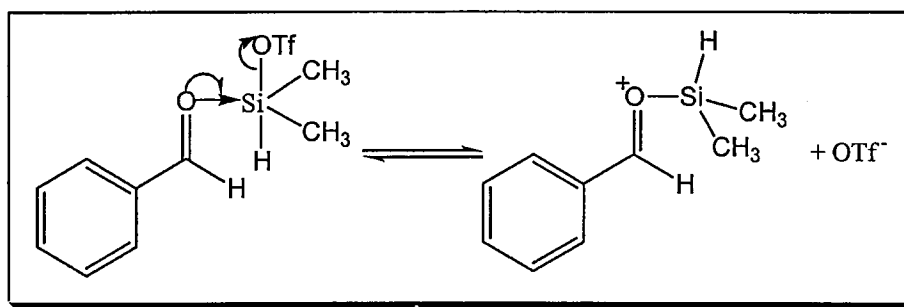
Thus, the higher the concentration of pentacoordinate silicon in this equilibrium, the greater the chance of hydride transfer. With this in mind we then carried out a range of experiments in the presence of anions that would react with such tetracoordinate silicon and thus favour the pentacoordinate species.

## **2.2-Reduction of aldehydes with $\text{Me}_2\text{HSiOTf}$ in chloroform in the presence of salts ( $\text{Bu}_4\text{N}^+\text{Y}^-$ where $\text{Y} = \text{OTf}$ ).**

### 2.2.1 Reduction of benzaldehyde.

The addition of  $\text{Me}_2\text{HSiOTf}$  to a range of aldehydes in the presence of salts was less reactive. Thus, the presence of added salts appears to slow down the reaction.

Benzaldehyde is readily reduced to give two main products, dibenzyl ether and benzyl alcohol. Thus, the use of the triflate salt not only leads to a less exothermic reaction but also enables a selective reduction to proceed. All the benzaldehyde was used up in this reaction, since there was no signal in the  $^1\text{H}$  NMR spectrum in the region of 9-10 ppm. The  $^1\text{H}$  NMR shows a single signal at 0.2 ppm corresponding to the two methyl groups of the silane. Since it is not a doublet, this confirms that the hydrogen of the silane is lost on reducing the benzaldehyde. Even in the presence of the salts a complex mixture is observed if the reaction is left for a couple of days. This suggests that the alcohol and ether undergo further reactions, presumably *via* carbocation formation. The proposed mechanism assumes that the pentacoordinate silicon can readily lose triflate and form a tetracoordinate species; so the addition of triflate ion forces the equilibrium back in favour of the pentacoordinate species (Scheme 12). It is the pentacoordinate species that transfers an hydrogen to effect the reduction.



Scheme 12

The calculated yields, by glc, are 80 % dibenzyl ether and 3 % benzyl alcohol.

### 2.2.2-Reduction of octanal

Octanal reacts with  $\text{Me}_2\text{HSiOTf}$  in the presence of the triflate salt in chloroform in a similar way to benzaldehyde. Octanal is more reactive than benzaldehyde. In fact, as we saw earlier, with octanal the reduction can occur in the absence of triflate. However, the presence of the salt leads to an increase in the yield of dioctyl ether, to 66 % (10 % octanol) instead of 27 % in its absence.

### 2.2.3-Reduction of trimethylacetaldehyde.

Trimethylacetaldehyde can also be reduced with  $\text{Me}_2\text{HSiOTf}$  in the presence of  $\text{Bu}_4\text{N}^+\text{OTf}^-$  giving the corresponding alcohol, neopentyl alcohol, and the corresponding ether, dineopentyl ether. The  $^{13}\text{C}$  NMR spectrum showed that the carbonyl group  $\text{C}=\text{O}$  had been reduced since the signal at 205.7 ppm, corresponding to the carbonyl, was replaced by a new signal at 81.63 ppm which corresponds to a  $\text{CH}_2$  next to an oxygen of an ether or alcohol. The yield of the reaction is not very high (ether, 44 %; alcohol, 15 %) because of the steric effect of the bulky  $\text{C}(\text{CH}_3)_3$  group. The remaining species is the unreacted aldehyde.

### 2.2.4-Reduction of 2-methylbutanal.

2-Methylbutanal gave the corresponding symmetric ether  $(\text{CH}_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2)_2\text{O}$  with a yield by gc of 47 %. The remaining products are the alcohol (12 %) and the aldehyde, which did not undergo a reaction.

### 2.2.5-Conclusions

In conclusion, in the presence of a triflate salt,  $\text{Me}_2\text{HSiOTf}$  selectively reduced all the aldehydes to the corresponding symmetric dialkyl ether. The yield depends on the nature of the alkyl group on the aldehyde, with bulky alkyl groups diminishing the yield of the reaction. The reaction was rapid and only a small amount of the corresponding alcohol was obtained (3-15 %). However, some unreacted aldehyde did remain.

RCHO (R = )	Ph	$(\text{CH}_2)_2\text{CH}_3$	$(\text{CH}_2)_4\text{CH}_3$	$(\text{CH}_2)_6\text{CH}_3$	$(\text{CH}_3)_3\text{C}$	$\text{CH}_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2$
$\text{Bu}_4\text{NOTf}$	80	57	61	66	44	47

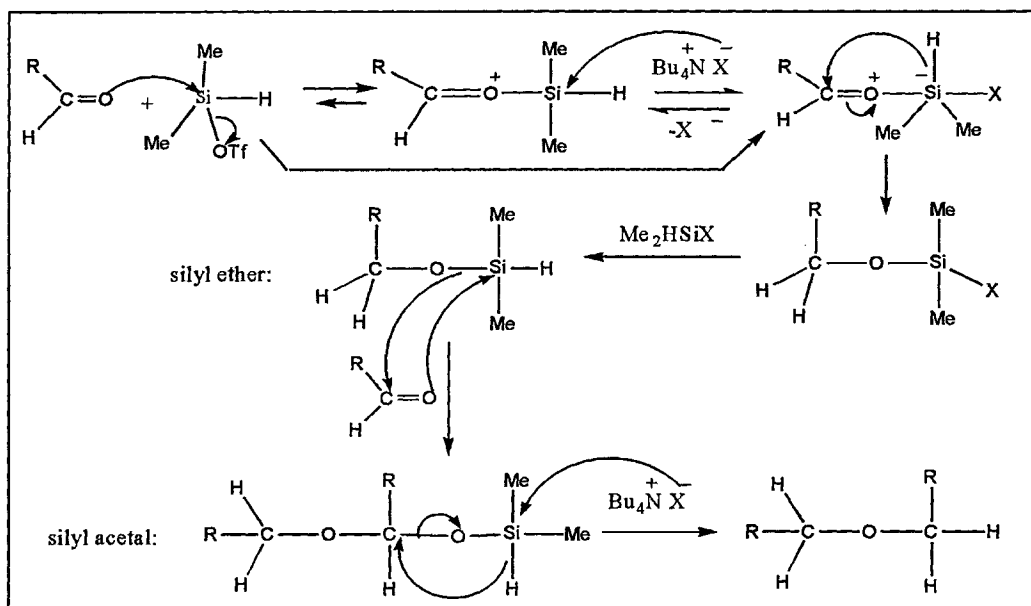
Table 3: Yields calculated by glc of the reduction reactions

### 2.2.6-Mechanism of the reduction reactions.

The first step is the coordination of the oxygen lone pair of the carbonyl group to the silicon atom to give a pentacoordinate species. This may involve loss of the triflate group; however, the anion of the salt can attack the silicon, leading back to the pentacoordinate silicon, where the silicon-hydrogen bond is activated. The following step is the “hydride transfer” of the hydrogen from the silicon to the carbon of the carbonyl group to give a silyl ether.

We believe that in the presence of unreacted  $\text{Me}_2\text{SiHOTf}$  an exchange of silicon species is observed giving an alkoxy-hydrosilane. This alkoxy-hydrosilane reacts with the aldehyde present in the mixture via an insertion. The oxygen of the alkoxy group attacks the carbon of the carbonyl and the oxygen of the carbonyl attacks the silicon atom. The last step of the reduction involves the nucleophilic attack of the salt to give a pentacoordinate species followed by

a hydride shift to give the symmetric dialkylether. This mechanism is shown in Scheme 13



**Scheme 13: Proposed mechanism of the reduction of aldehydes.**

A series of experiments was subsequently carried out to test this mechanism including:

- using two different aldehydes with a silane
- mixing aldehydes and silanes with alcohols or silanols
- reacting a dialkoxysilane in the presence of salts
- starting with two alkoxy-hydrosilanes
- using one aldehyde and an alkoxy-hydrosilane with the same or different alkyl group.

All these experiments will be explained later in this thesis. (sections 2.5, 2.6, 2.7 and 2.8)

### 2.3-Reduction of aldehydes with $\text{Me}_2\text{HSiOTf}$ in the presence of $\text{Bu}_4\text{N}^+\text{Y}^-$ ( $\text{Y}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) in chloroform.

A range of others salts were used to test the applicability of this reaction. Thus tetrabutylammonium chloride, bromide and iodide were reacted, separately, with  $\text{Me}_2\text{HSiOTf}$  and aldehydes.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies were performed in deuteriochloroform to follow the reactions. A similar set of results to those observed with triflate ion were obtained.

$\text{RCOH (R=)}$	Ph	$(\text{CH}_2)_2\text{CH}_3$	$(\text{CH}_2)_4\text{CH}_3$	$(\text{CH}_2)_6\text{CH}_3$	$(\text{CH}_3)_3\text{C}$	$\text{CH}_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2$
$\text{Bu}_4\text{NCl}$	67	49	51	54	31	33
$\text{Bu}_4\text{NBr}$	43	41	46	48	25	27
$\text{Bu}_4\text{NI}$	41	37	40	40	12	17

**Table 4: Yields % by glc of the reductions using different salts**

A comparison of the yields of the different reactions with the different salts confirmed that the reduction depends upon the nature of the salts.

For example, with the reduction of the benzaldehyde, the triflate salt is the most effective (yield of ether = 80 %), follow by the chloride and bromide (yield of ether = 67 and 43 %) and the least effective is the iodide salt with a yield of 41 %.

For the other aldehydes the results were similar, giving the same order for the effectiveness of the salts  $\text{OTf} > \text{Br} > \text{Cl} > \text{I}$  (this is probably explained by readiness of these halides to form pentacoordinated species).

Using different salts again showed that a bulky alkyl group lowered the yield and that the ether and the alcohol are converted into a complex mixture if the reaction mixture is left in the presence of salts for a long period.

Since the reaction in the presence of other ions leads to pentacoordinate species involving ligands other than triflate, different dimethylhalosilanes were employed to examine whether more readily available reagents could be employed in this reduction.

#### **2.4-Reduction of aldehydes with $\text{Me}_2\text{HSiX}$ where X = chloride in chloroform.**

$\text{Me}_2\text{HSiOTf}$  is not commercially available and its synthesis is difficult.

On the contrary,  $\text{Me}_2\text{SiHCl}$  is commercially available and thus we examined its use in the reduction reaction. The reactions with aldehydes gave the same kind of results as with the silyl triflate, except that the yields were lower than those obtained with the silyl triflate.

##### **2.4.1-Reduction of benzaldehyde**

In the presence of  $\text{Me}_2\text{SiHCl}/\text{Bu}_4\text{NCl}$  benzaldehyde is reduced to dibenzyl ether and benzyl alcohol; however, there was still an appreciable amount of the benzaldehyde at the end of the reaction. This suggests that  $\text{Me}_2\text{HSiCl}$  is not reactive enough to reduce all the aldehyde. We obtained the maximum percentage conversion, 42 %, using two equivalents of silane. The yield does not improve if the reaction is repeated with an excess of the salt. Benzaldehyde remained in the mixture even if the reaction was left longer.



#### 2.4.2-Reduction of other aldehydes.

Octanal was reacted with the dimethylchlorosilane (2 molar excess)

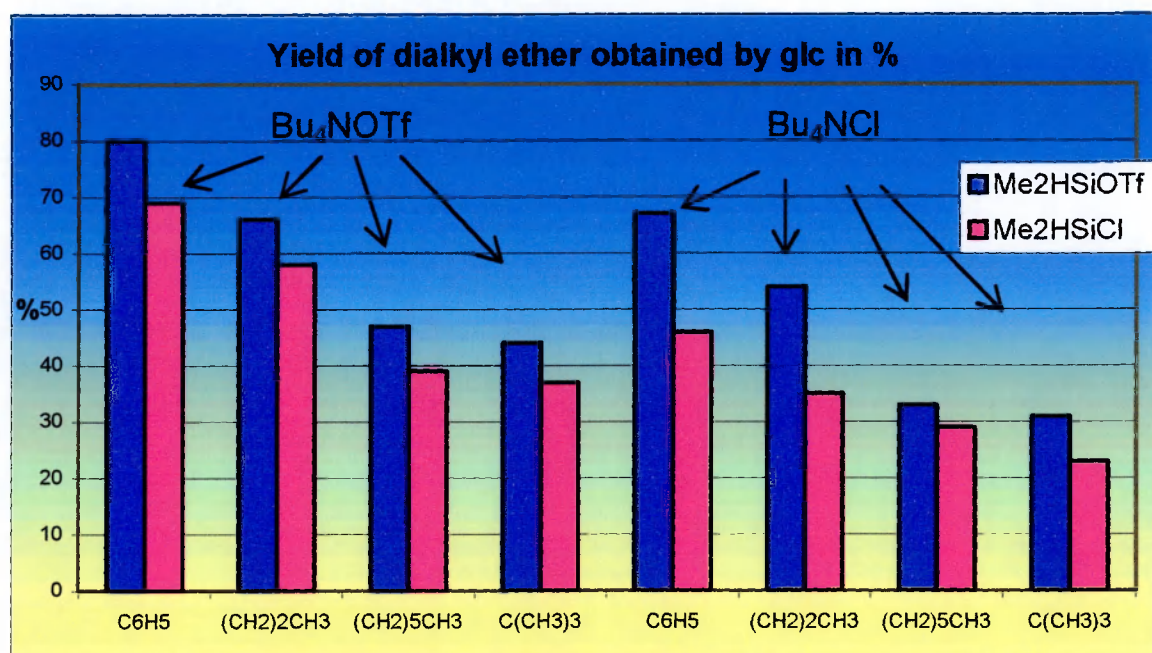
/ammonium salts to give the corresponding ether (dioctyl ether) and the corresponding alcohol (octyl alcohol) in a combined yield of 33 %.

2-Methylbutanal was also reduced by dimethylchlorosilane to give the 2-methylbutyl ether and 2-methylbutanol. The yield of ether was 30 %.

Trimethylacetaldehyde was reduced to di-neopentyl ether and alcohol, the yield of formation of ether was 26 % in the presence of salts.

We believe that aldehydes are reduced by dimethylchlorosilanes in the same way that they are reduced by dimethylsilyltriflates, only the yield is reduced.

We tried to increase the yield using 2 equivalents of chlorosilane, leaving the reactions for much longer and also by carrying them out under reflux. However, the yields did not change, we always had some aldehyde left in the reaction mixture. The yields are summarised in Graph 1.



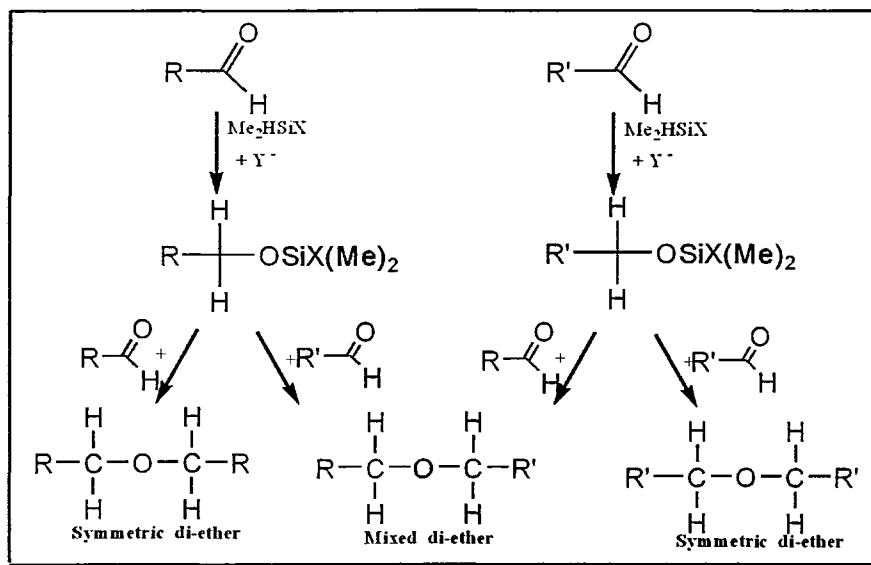
**Graph 1: Summary of yields (by glc) of ether synthesis during the reaction with Me<sub>2</sub>HSiCl and Me<sub>2</sub>HSiOTf with RCHO in presence of Bu<sub>4</sub>NY (where Y = OTf or Cl.)**

The change of the dimethylhalosilane from OTf to Cl shows that the triflate is the more efficient. The effect of different salts on the outcome is the same when we use different silanes, Me<sub>2</sub>HSiX. The order of efficiency of the salt does not change: triflate is a better promoter of the reduction reaction than chloride. The different reactivity of the aldehydes is again due to the bulk of the alkyl group.

### **2.5-Reduction of a mixture of two different aldehydes with Me<sub>2</sub>HSiOTf in the presence of nucleophiles in chloroform.**

The reduction of a single aldehyde by Me<sub>2</sub>HSiOTf in the presence of nucleophiles has been discussed in the previous section. With aldehydes, the corresponding symmetric ether is the main product. In order to study the mechanism of this reaction, the reduction of a mixture of two different

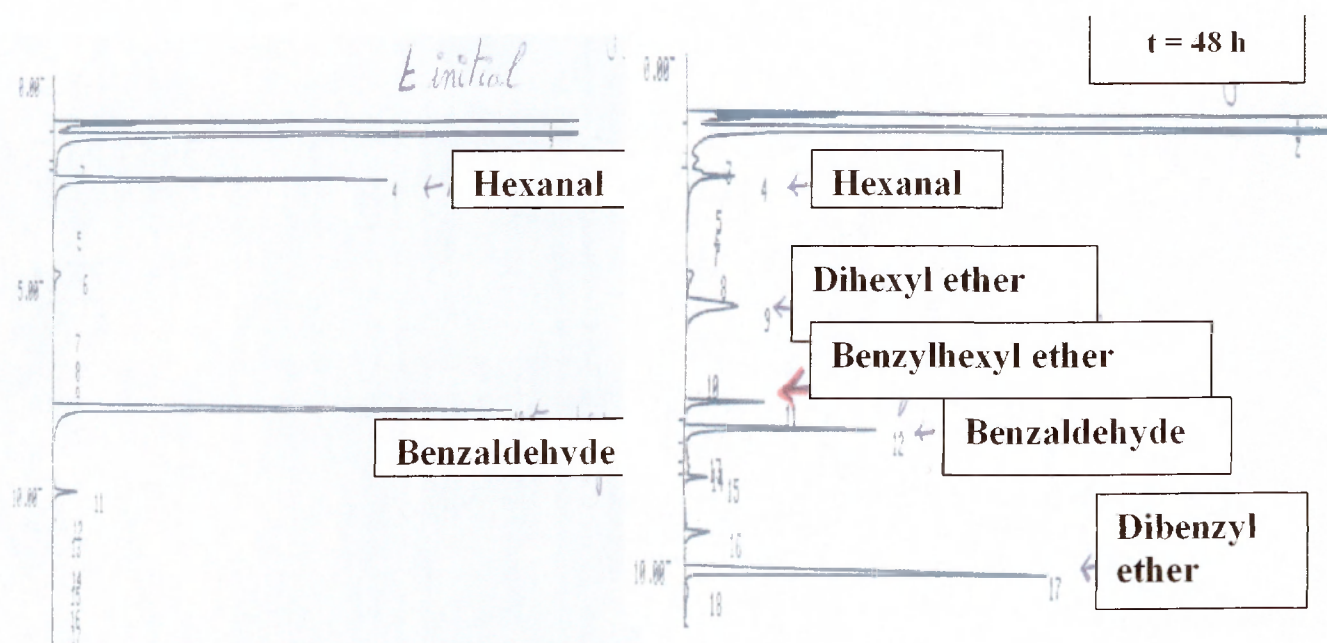
aldehydes was carried out. The objective of this reaction was to examine whether symmetrical ethers would be obtained or a statistical mixture of all three ethers: the two symmetric ethers and the mixed ether, with the corresponding ratio of 1:1:2.



**Scheme 14: Formation of symmetric and mixed ethers starting with two different aldehydes**

#### 2.5.1-Reduction of benzaldehyde and hexanal.

An equimolar mixture of hexanal and benzaldehyde was reacted with  $\text{Me}_2\text{HSiOTf}$  in the presence of salt in chloroform. The result of this reaction is a mixture of different ethers and alcohols corresponding to reduction of the starting materials, namely benzaldehyde and hexanal. One new product is formed during the reaction. Analysis of this new product by NMR spectroscopy shows two signals at 3.52 ppm and 4.43 ppm, corresponding to the  $\text{OCH}_2$  of the mixed ether  $\text{PhCH}_2\text{-O-CH}_2(\text{CH}_2)_4\text{CH}_3$ . We also followed this reaction by gas chromatography, with xylene as the internal standard, to examine the yields of the various ethers and how they change during the reaction.



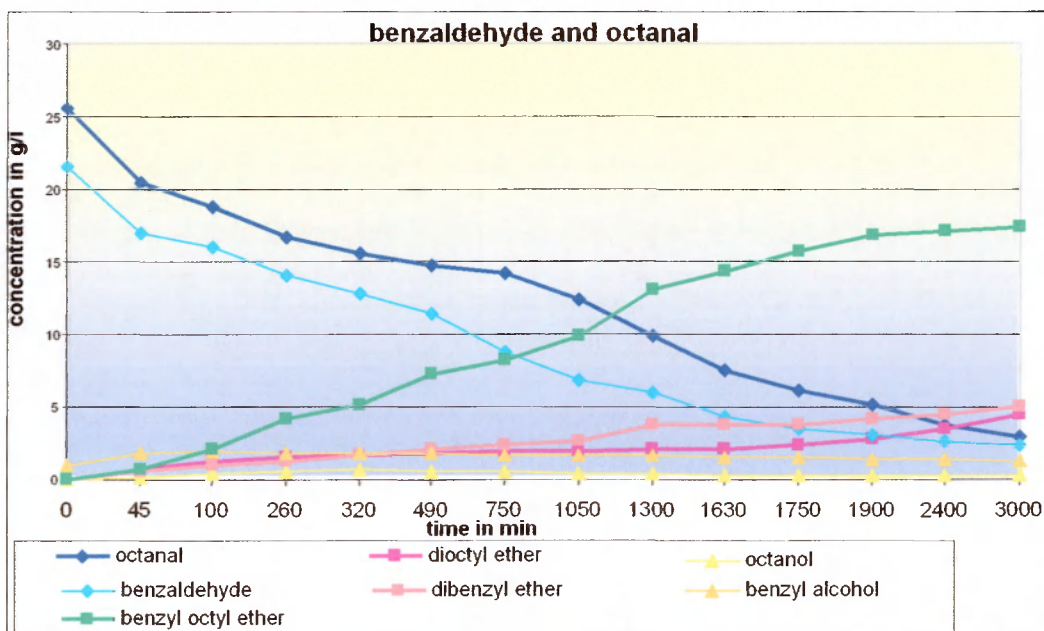
**Figure 6: Gas chromatograms at the beginning ( $t = \text{initial}$ ) and at the end ( $t = 48 \text{ h}$ ) of the reduction reaction.**

In Figure 6 we see that at the start of the reaction ( $t = \text{initial}$ ) we can see two major signals, one corresponding to the hexanal with a retention time of 2.4 min and one signal corresponding to the benzaldehyde at 7.8 min. This initial time corresponds to the time taken to prepare the sample and inject the mixture. This does show the beginning of the formation of products, as we can see small signals corresponding to the symmetric ethers. The tallest of these product signals (giving the highest yield calculated using *o*-xylene as standard) with a retention time of 10.4 min corresponds to the dibenzyl ether, which proves again that benzaldehyde is more reactive than hexanal. We could also observe the formation of some dihexyl ether (Retention time = 4.8 min), but no trace of the mixed ether, benzyl hexyl ether. It appears that the two symmetric ethers are formed preferentially at the beginning of the reaction.

At the end of the reaction, it was clear that the two signals corresponding to the starting materials had decreased and this was accompanied by an increase in the two signals corresponding to symmetric ethers, dibenzyl and dihexyl ether with yields of 21 % and 16 % respectively. We also see the formation of a new signal from the mixed benzyl hexyl ether, in 37 % yield. The experimental ratio matches the theoretical ratio 1:2:1 from the statistical distribution for symmetric: mixed: symmetric ethers. Any deviation arises from the difference in the reactivity of the aldehydes towards the reduction.

### 2.5.2-Reduction of benzaldehyde and octanal.

Another reaction was carried out using benzaldehyde and octanal, but this time we followed the reaction with time by gas chromatography. Graph 2 shows how the concentration of reagents and products change with time.



**Graph 2: Reduction of benzaldehyde and octanal with  $\text{Me}_2\text{HSiOTf}$  in the presence of a nucleophiles followed by gas chromatography.**

The graph shows a clear correlation between the loss starting material and the build up of product and in particular:

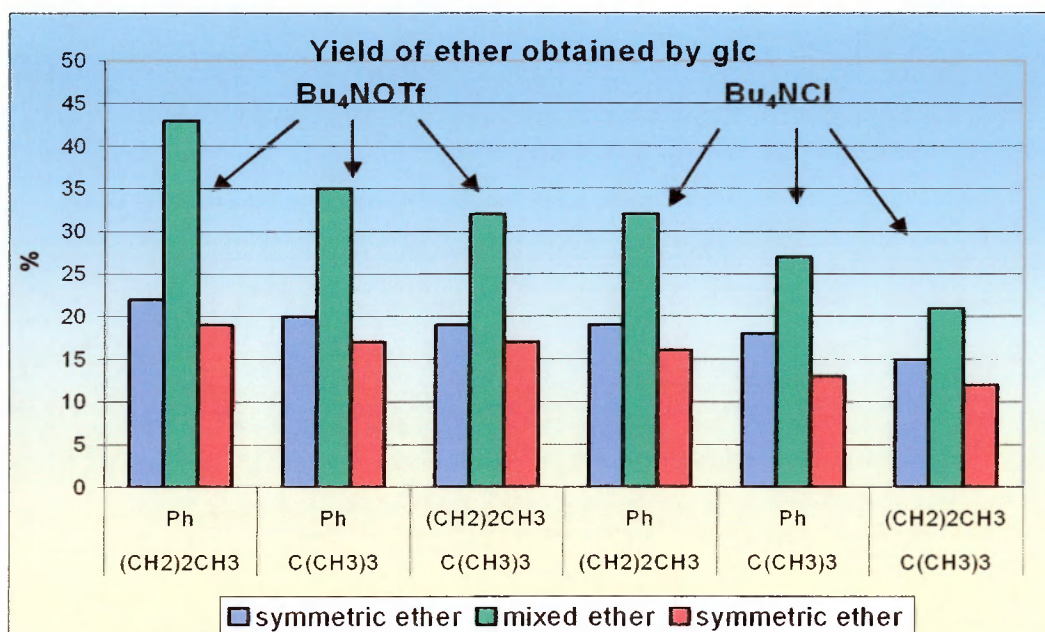
- a decrease in the concentration of the benzaldehyde and octanal such that only 9 % and 5 % remain after 3000 min;
- an increase in the concentration of the corresponding dibenzyl and dioctyl ether, to give yields of 23 % and 14 %;
- formation of the benzyl octyl ether, which increases during the reaction to give 46 % yield.

The benzyl and octyl alcohols gave about 5 % and 10 % final yield respectively. We believe that the alcohol is an intermediate in these reactions; during the reaction the alcohol  $RCH_2OH$  is formed and used by the  $Me_2HSiCl$  to form a new complex  $Me_2HSiOCH_2R$ , which then reacts with one of the aldehydes to give the symmetric or mixed ether as product. After 2000 min we can consider the reaction as effectively finished as the formation of ether is irreversible, even though we still have some aldehyde remaining.

### 2.5.3-Reduction of others aldehydes.

Others experiments gave similar results as shown in Graph 3:





**Graph 3: Summary of yields (by glc) of ethers obtained in the reduction of aldehydes RCHO and R'CHO with Me<sub>2</sub>HSiCl in the presence of BuN<sub>4</sub>OTf or BuN<sub>4</sub>Cl**

Bu<sub>4</sub>NOTf is more efficient than Bu<sub>4</sub>NCl irrespective of the types of aldehyde used for the reduction reaction. When using benzaldehyde and butanal, the reaction gave 22 % of dibenzyl ether, 19 % of dibutyl ether and 44 % of benzyl butyl ether. The reaction of benzaldehyde and trimethylacetaldehyde afforded 20 % of dibenzyl ether, 16 % of di<sup>i</sup>butyl ether and 35 % of the mixed benzyl <sup>i</sup>butyl ether. If we compare the yields of these two systems we can detect a decrease in yield when the trimethylacetaldehyde is used. This is probably due to the presence of a bulky alkyl group as observed using only one aldehyde, leading to a reduction in reactivity. The steric bulk only affects the yield of the ethers involved, which are the di<sup>i</sup>butyl ether and the mixed ether.

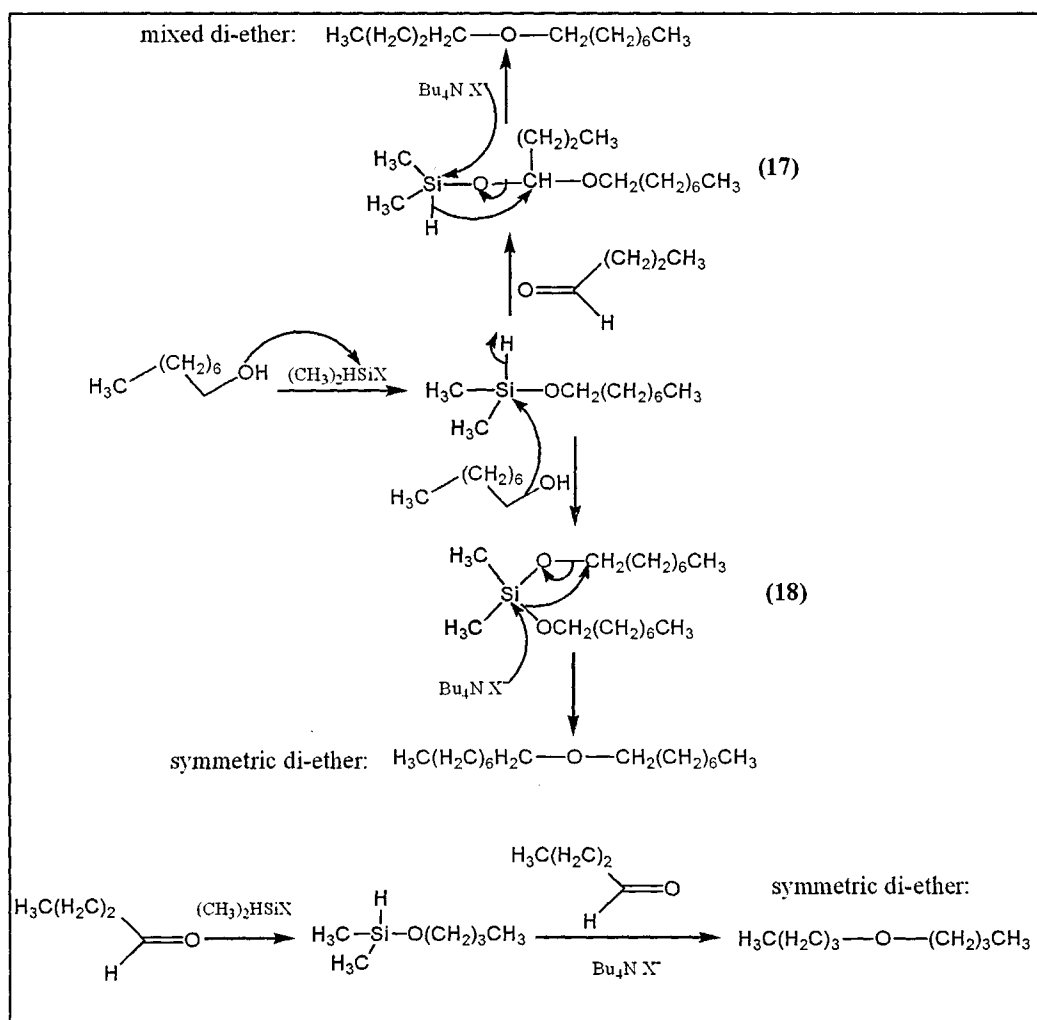
If we work with even less reactive aldehydes, such as butanal and trimethylacetaldehyde, the yields are even smaller, providing 18 % dibutyl ether, 16 % di<sup>i</sup>butyl ether and 32 % of butyl <sup>i</sup>butyl ether. We had thought that working with a less reactive aldehyde would encourage the selective formation

of either the symmetric ether or the mixed ether. However, the reaction is observed to slow down in all cases, increasing the amount of aldehydes remaining in the mixture.

## **2.6-Reduction of aldehyde and alcohol together in the presence of $\text{Me}_2\text{HSiX}$ and salt.**

In order to understand the mechanism of the reaction and to understand the factors that control the regioselectivity of the reduction, reactions were carried out in the presence of various other starting materials. For example, an aldehyde  $\text{RCHO}$  was mixed with an alcohol  $\text{R}'\text{CH}_2\text{OH}$ , where  $\text{R}$  is a different group to  $\text{R}'$ . A possible mechanism for this reaction is given in Scheme 15:





**Scheme 15: Mechanism of the reduction of aldehyde and alcohol together in the presence of  $\text{Me}_2\text{HSiX}$  and salt.**

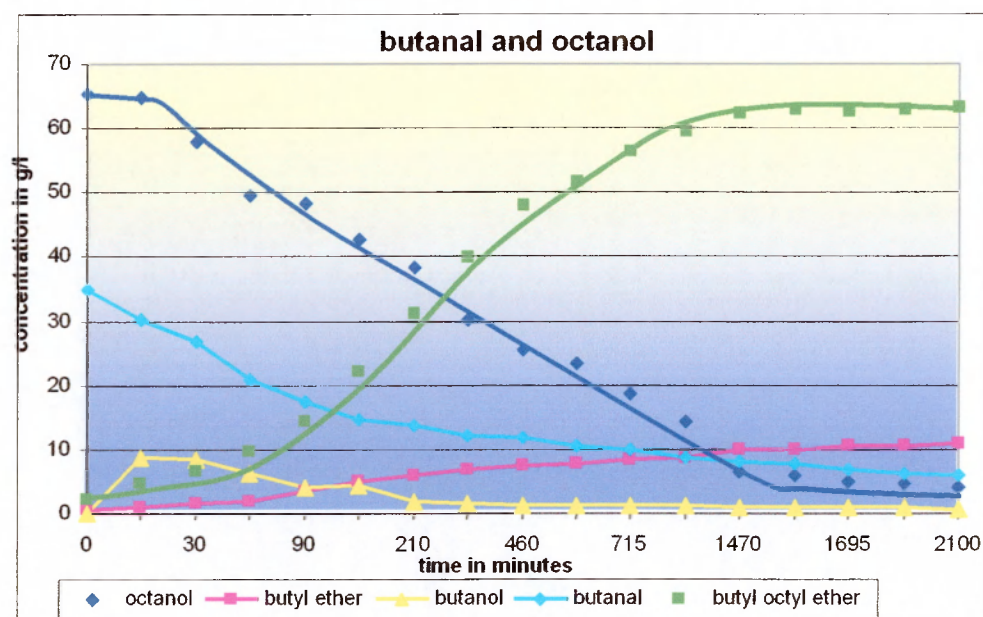
The proposed mechanism of the reaction suggests the formation of the mixed ether and the formation of two symmetric ethers: one corresponding to the alcohol and one coming from the aldehyde.

The formation of the mixed ether is due to attack of the oxygen of the alcohol at the silicon atom, giving the dimethylhexyloxyhydrosilane, which can react in two ways. First by acting as a reducing agent with the aldehyde, whereby the oxygen of the aldehyde attacks the silicon of the alkoxyhydrosilane and the oxygen of the alkoxyhydrosilane attacks the carbon of the carbonyl, giving the

acetal intermediate (17). The subsequent step has already been described in the reduction of one aldehyde and affords the mixed ether in this example.

Secondly, the alkoxyhydrosilane can react with the alcohol present in the solution, to give a dialkoxysilane (18), which can be attacked by the salt and rearranged to give the symmetric dihexyl ether. Finally the other symmetric ether can be obtained by the previously described reduction of one aldehyde using  $\text{Me}_2\text{HSiOTf}$  and  $\text{Me}_2\text{SiCl}$ . The reaction was carried out using butanal and octanol to see if the proposed mechanism matches the experimental result.

Results of the reaction are shown in Graph 4:



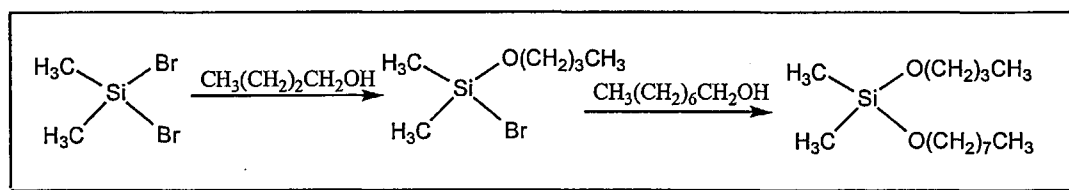
**Graph 4: Reduction of butanal and octanol with  $\text{Me}_2\text{HSiOTf}$  and  $\text{Me}_2\text{SiCl}$  followed by gas chromatography.**

The reaction shows the exponential decrease of the two starting materials: butanal and octanol. The reaction shows the formation of the mixed ether as the major product, with a percentage yield equal to 70 %. We can also observe the formation of the symmetric dibutyl ether in a smaller amount (17 %), but we do not form the symmetric dioctyl ether as was predicted by the proposed

mechanism. Comparing the percentages of the different products we can conclude that the alcohol reacts more quickly with the  $\text{Me}_2\text{HSiOTf}$  than the aldehyde, to give the alkoxyhydrosilane. This then reacts with the aldehyde to give the silyl acetal which subsequently formed the predominant mixed ether. These results suggest two further reactions that could test this mechanism: firstly, the reaction of a dialkoxysilane in the presence of salt and, secondly, the reaction of an alkoxyhydrosilane with an aldehyde.

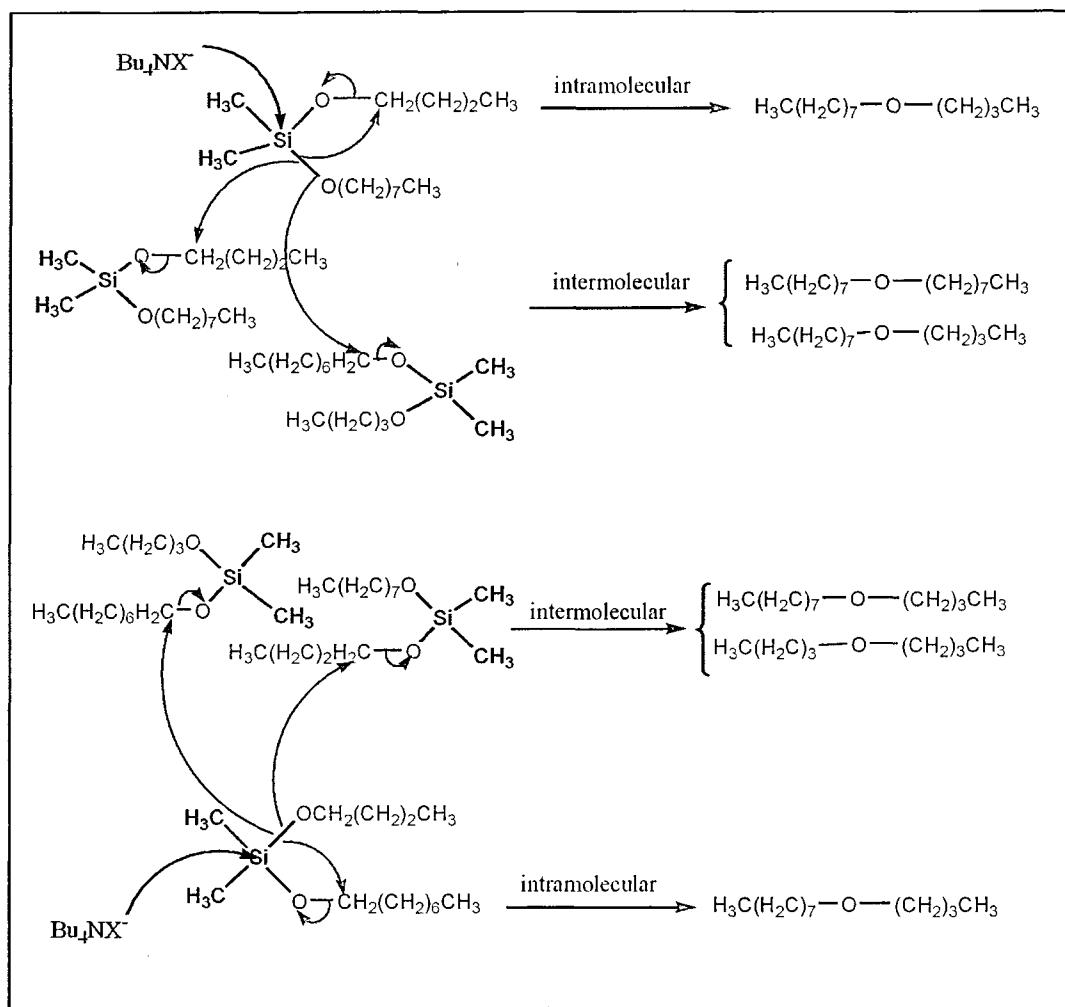
### 2.7-Reaction of a dialkoxysilane with a nucleophilic salt.

Dialkoxysilanes were prepared by reacting dibromodimethylsilane with two equivalents of alcohol, as describe in Scheme 16. The resulting mixture was distilled to remove any of the symmetrical dialkoxysilane.



**Scheme 16: Formation of dialkoxysilanes**

The possible outcomes of the reaction of butoxyoctyloxydimethylsilane with  $\text{Bu}_4\text{NF}$  or  $\text{Bu}_4\text{NBr}$  are shown in Scheme 17.



**Scheme 17: Possible mechanism for the formation of symmetric and mixed ethers starting with a dialkoxysilane.**

Tetrabutylammonium chloride can activate the silicon species, leading to the liberation of the nucleophilic octanoxide group. This can react intramolecularly, the oxygen of the octanoxo group attacking the carbon of the butyl group to give the mixed ether or it can proceed intermolecularly:

1) If the oxygen of the octyloxy group attacks the carbon of another octyl group present on another dialkoxysilane in the mixture, then the dioctyl ether is obtained.

2) If the oxygen of the octyloxy group attacks the carbon of a butyl group present on another dialkoxysilane in the mixture, then the mixed butyloctyl ether is formed.

The statistical ratio for these two products is 2:1 for mixed: symmetric diether respectively.

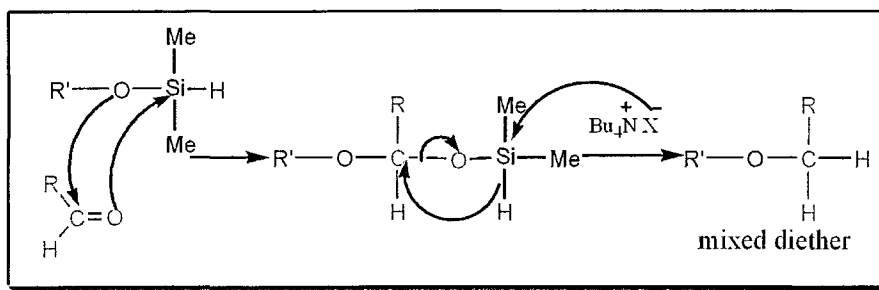
If the butoxy group acts as a nucleophile instead of the octyloxy group similar sets of products are obtained. If the oxygen of the butoxy attacks the carbon of the octyl group on the same dialkoxysilane, the mixed diether is obtained. The intermolecular products will be the symmetric butyl diether or the mixed ether again in an overall ratio of 2:1 for mixed: symmetric di-ethers.

We followed this reaction by  $^1\text{H}$  NMR spectroscopy, which showed two signals at 2.91 and 3.44 ppm, which were triplets corresponding to the hydrogens of the two alkoxy  $\text{CH}_2$  groups close to the silicon atoms in the starting material:

$\text{SiOCH}_2(\text{CH}_2)_6\text{CH}_3$  and  $\text{SiOCH}_2(\text{CH}_2)_2\text{CH}_3$ . Leaving the reaction overnight did not give any ether, as was observed in part 2.6. Thus, the intramolecular or intermolecular rearrangements are not possible with the dialkoxysilane, even in the presence of a salt nucleophile.

## **2.8-Reduction of an aldehyde in the presence of an alkoxyhydrosilane.**

In this part we used an alkoxyhydrosilane as the reducing agent. The silicon-hydrogen bond can be activated with nucleophiles by attack at the silicon atom, which provides the formation of a hydride-like species. Since the alkoxyhydrosilane is thought to be an intermediate in the reaction, we would hope that by providing a different type of aldehyde we would end up only forming a mixed ether, as shown in Scheme 18.

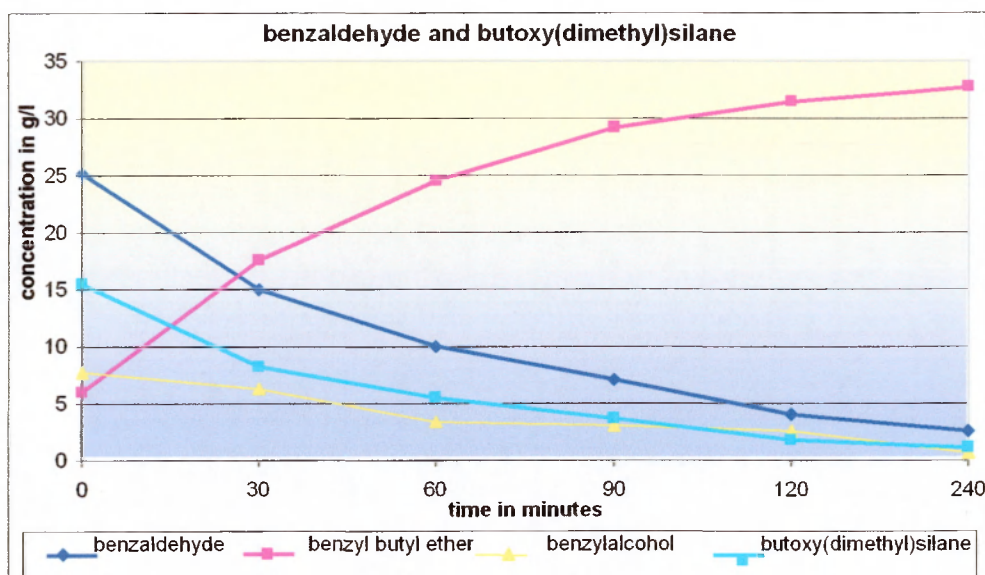


**Scheme 18: Possible mechanism for an exclusive formation of mixed ethers**

The oxygen of the carbonyl attacks the silicon atom and the oxygen of the alkoxy attacks the carbon atom of the carbonyl. Then the alkoxyhydrosilane is attacked by the anion of the salt, which forms the pentacoordinate silicon species, where the silicon-hydrogen is activated. The last step is the transfer of the hydride to the acetal carbon atom. The reaction ends up forming the mixed di-ether together with the dialkylsiloxane.

#### 2.8.1-Reduction of benzaldehyde using dimethylbutoxysilane.

The reduction reaction was carried out using dimethylbutoxysilane as a reducing agent with benzaldehyde in the presence of a salt. Again the reaction was followed by gas chromatography as shown in Graph 5.



**Graph 5: Reduction of benzaldehyde with butoxy(dimethyl)silane.**

At the beginning of the reaction we detected a large concentration of the two starting materials: dimethylbutoxysilane and benzaldehyde. These concentrations then decrease exponentially from time equals zero to 120 min. After 120 min the concentrations are still decreasing but at a lower rate. Simultaneously, we can see the formation of the mixed benzyl butyl ether as the only ether product. No trace of the dibenzyl and dibutyl ether was detected. Some benzyl alcohol was formed between 0 and 100 min, due to the presence of water in the salt; however, the concentration then decreases as it is consumed during the reaction. Our results suggest that alkoxyhydrosilanes are very efficient reducing agents for the reduction of aldehydes and form exclusively the mixed ether under mild conditions. This then provides a non-basic alternative to the Williamson ether synthesis. The retro-synthetic analysis showed that the mixed ether  $R'CH_2OR$  came from the addition of an aldehyde  $R'CHO$  with an alcohol  $ROH$ . So the synthetic methodology to obtain the mixed diether was to react an alcohol  $ROH$  with  $Me_2HSiX$  to give  $ROSi Me_2H$  which then it is reacted with the aldehyde  $R'CHO$  in the presence of salt.

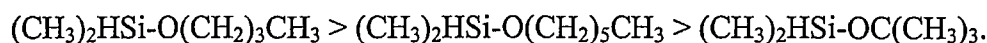
### 2.8.2-Reduction of a range of aldehydes using alkoxyhydrosilanes.

A series of experiments was carried out using aldehydes, which were reduced by a series of different alkoxyhydrosilanes. This enabled us to investigate how the alkyl group on the aldehyde or the alkoxy group on the silicon species affects the selectivity of ether formation.

RCHO (R=)	Ph	Ph	Ph	(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>
R'O-HSiMe <sub>2</sub> (R'=)	(CH <sub>2</sub> ) <sub>3</sub> CH 3	(CH <sub>2</sub> ) <sub>5</sub> CH 3	C(CH <sub>3</sub> ) <sub>3</sub> 3	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>
Bu <sub>4</sub> NCl	85	81	68	80	44

**Table 5: Yields by glc of non-symmetric dialkyl ethers obtained in the reduction of aldehydes using alkoxyhydrosilanes.**

In all cases the mixed diethers are obtained as the only ether product. The chemoselectivity is very good even when less reactive reagents were employed. If we compare the results obtained in the three first columns, the benzaldehyde is reacting with three different alkoxyhydrosilanes: dimethyl(butoxy)silane, dimethyl(hexyloxy)silane and dimethyl(<sup>t</sup>butoxy)silane. The yield of the mixed ethers decreases when a bulkier alkoxy group is attached to the reducing agent, from 85 to 68 %. So the efficiencies of the alkoxyhydrosilanes are in the following order:



Comparing now entry 2 with entries 4 and 5, the yield stays the same when we go from an aryl group to a primary alkyl group but decreases when using a bulky alkyl group on the aldehyde; from 81 to 44 %.



## **2.9-Reduction of aldehydes with $\text{Me}_2\text{HSiX}$ , where $\text{X} = \text{OTf}$ , $\text{Cl}$ , in chloroform in the presence of an Amberlyst resin.**

One of the problems of using tetrabutylammonium salts is that they are difficult to remove at the end of the reaction. Repeated washing to remove the ammonium salts led to the loss of the ether and alcohol product. Thus, an Amberlyst resin was used to provide the nucleophilic species since this can be easily removed at the end of the reaction. The Amberlyst polymer is a tetraalkylammonium resin with anions on the surface such that it can react in heterogeneous manner. We used the bromide and chloride polymer supported versions of Amberlyst. It was added to the aldehydes in the presence of  $\text{Me}_2\text{HSiX}$  where  $\text{X} = \text{OTf}$  and  $\text{Cl}$ .

### **2.9.1 –Reduction of aldehydes using bromide Amberlyst polymers and silanes as reducing agent.**

- Reduction of benzaldehyde

Benzaldehyde was completely converted to dibenzyl ether and benzyl alcohol. The yield of the reaction was 65 % for the formation of the ether when using dimethylsilyltriflate as the reducing agent. The yield is decreased compared to that of the free salt because of the availability of the nucleophile, even when all the ether was extracted by using a Soxhlet. The key signal in the  $^1\text{H}$  NMR spectrum of the dibenzyl ether is at 4.3 ppm (s, 2H,  $\text{CH}_2$ ) and in the  $^{13}\text{C}$  NMR spectrum at 71.4 ppm (t,  $\text{CH}_2\text{O}$ ).

- Reduction of others aldehydes using bromide polymer and dimethyl silyl triflate.

Octanal is reduced to dioctyl ether and octyl alcohol. The yield of the ether is 63 % and the yield of the octanol is less than 10 %.

Trimethylacetaldehyde gave the dineopentyl ether and neopentyl alcohol with yields of 42 and 12 % respectively. Finally, 2-methylbutanal gave the corresponding ether in a good yield (60 %) and 2-methylbutanol (8 %).

RCHO (R=)	Ph	(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>3</sub> C	CH <sub>3</sub> CH(C <sub>2</sub> H <sub>5</sub> )
(X=I) Me <sub>2</sub> HSiX						
OTf	65	51	58	63	42	60
Cl	40	29	33	36	18	26

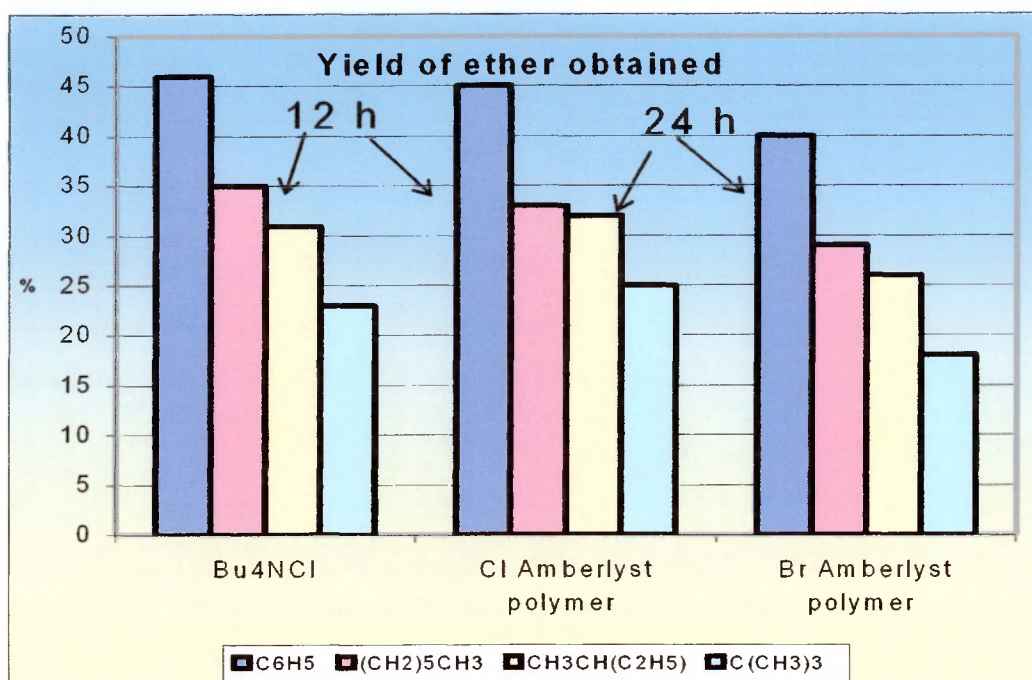
**Table 6: Yield by glc of the diether produced by the reaction of an aldehyde RCHO with Me<sub>2</sub>HSiX and Bromine Amberlyst resin**

As expected we observed a reduced yield of ethers if the chlorosilane was employed. These experiments confirm that the silyl triflate is the best reducing agent; however, the silyl chloride is efficient enough to give about 40 % of the diether. If we compare the results obtained with the Bu<sub>4</sub>NBr salt and the bromide Amberlyst resin, we can see that the salt is more effective in term of the syntheses of the ether than the amberlyst. This is probably due to the availability of the nucleophile in solution. The Bu<sub>4</sub>NBr salt can dissolve in the solvent with the others reagents (aldehyde, dimethylhalosilane), so we end up with a homogeneous solution. However, the Amberlyst resin is a solid, such that the bromide ions are available on the surface of the Amberlyst and reaction only occurs if there is a good exchange between the reagents present in solution and the Amberlyst surface; that is, we effectively have a heterogeneous

reaction. If we leave the reaction for longer the yield is improved, due to the degradation of the Amberlyst, which liberates more bromide ions in the solution. This small amount of nucleophile now present in solution can permit a homogenous reaction and increase the yield of formation of ether.

#### 2.9.2-Reduction of aldehydes using chloride Amberlyst polymer.

Chloride Amberlyst polymer was also used as a nucleophile for the reduction of aldehydes in the presence of dimethylchlorosilane. We again expect similar results to the free salt, in that chloride ion on the surface of the polymer will attack the silicon and activate the silicon-hydrogen bond. The results are summarised in Graph 6 where we compare the reactivity of the chloride salt, the chloride Amberlyst polymer and also the bromide Amberlyst polymer.



**Graph 6: Summary of yields of diether obtained in the reduction of aldehydes with Me<sub>2</sub>HSiCl in the presence chloride salt, chloride and bromide polymer amberlyt.**

Comparing first the yields obtained using chloride and bromide Amberlyst polymers, we can see that the chloride Amberlyst polymer is more effective than the bromide, as observed with the salt. Dibenzyl ether was obtained in 45 % yield and 40 % yield respectively for the chloride and bromide Amberlyst polymers. Now looking at the yields obtained for the chloride salt and the Amberlyst polymer, we can see the same pattern for the different aldehydes but with different reaction times. Using the salt allowed a faster reaction; 12 h for the salt compared to 24 h for the polymer. This is may be due to the availability of the nucleophile in solution. All the experiments were stirred vigorously, since good stirring will promote the contact between the anion on the surface and the reagent; nevertheless, the reaction is slower because it involves a heterogeneous reaction.

## 2.10-Reduction of ketones, $R_1R_2C=O$ , with $Me_2HSiOTf$ in chloroform under different conditions.

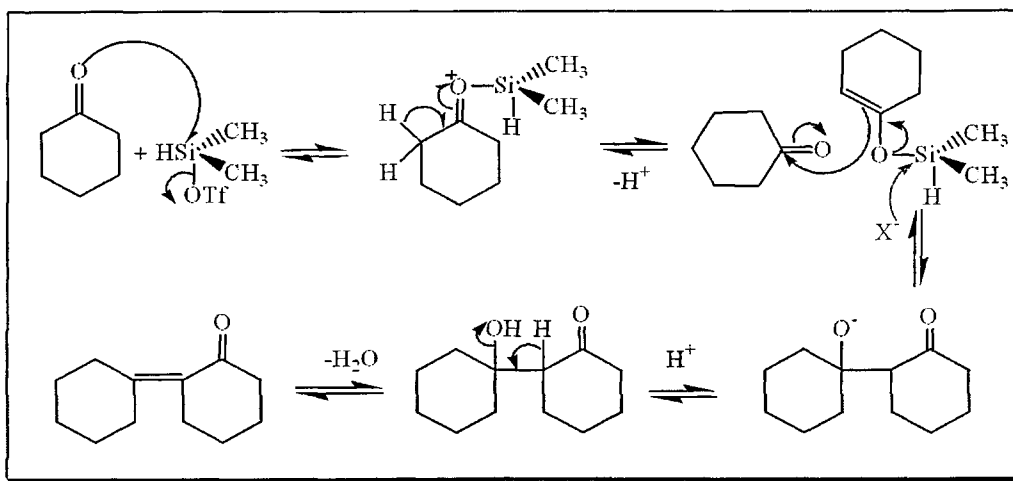
### 2.10.1-Reduction of ketones with $Me_2HSiOTf$ in chloroform.

The reduction of ketones by  $Me_2HSiOTf$  in chloroform was carried out in the same way as with the aldehydes. The reduction is difficult to perform because it is slower and gives a more complicated array of products. The reaction was carried out at room temperature or sometimes at reflux for several hours. In these cases,  $^1H$  and  $^{13}C$  NMR spectroscopy were used to follow the reduction reaction as it was not possible to find a gas liquid chromatography column that could measure both the loss of the ketones and the formation of the volatile ethers.

- Reduction of cyclohexanone with  $Me_2HSiOTf$  in chloroform.

The reaction of cyclohexanone with  $Me_2HSiOTf$  at room temperature produced a large number of products. It was clear that an aldol reaction had occurred giving the enone as the main product, as illustrated in Scheme 19.

This aldol product was characterised by  $^{13}C$  NMR spectroscopy which showed a total of 10 signals for the different carbons. The reaction did not go to completion since cyclohexanone, the starting material, was still present in the final mixture. The reaction was repeated with 2 equivalents of  $Me_2HSiOTf$  but still gave the same result.



**Scheme 19: The alternative aldol reaction.**

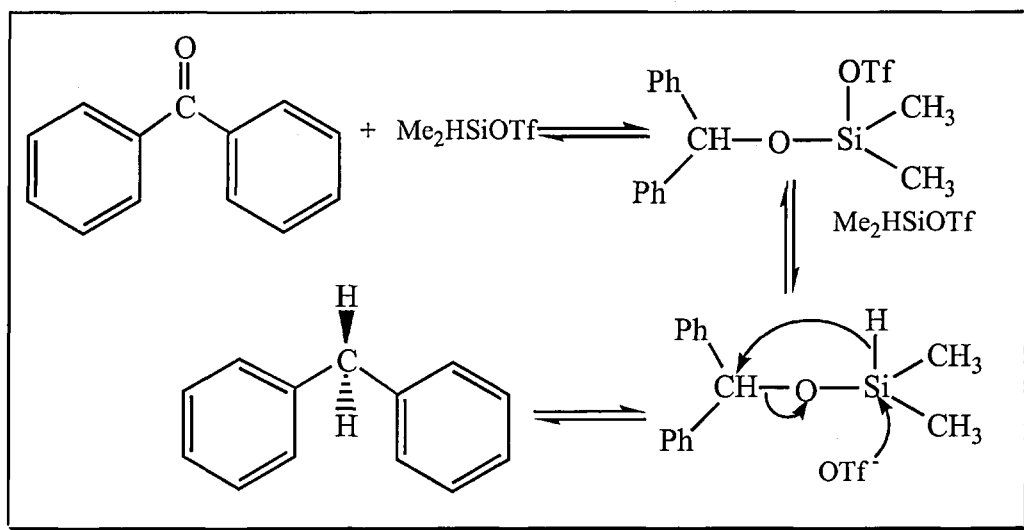
As with the aldehyde, the first step is the attack of the oxygen of the ketone at the silicon atom. Instead of forming a pentacoordinate silicon in which the silicon-hydrogen bond is activated, the loss of the most acidic proton  $\alpha$ - to the carbonyl group forms the silylenol ether. Nucleophilic attack of this enol at the cyclohexanone followed by loss of water then gives the final aldol product.

- Reduction of acetophenone with  $\text{Me}_2\text{HSiOTf}$  in chloroform.

Acetophenone and  $\text{Me}_2\text{HSiOTf}$  react in the same way as cyclohexanone, to give the aldol product  $\text{PhCOCH}=\text{CPh}(\text{CH}_3)$ . This was characterised by  $^1\text{H}$  NMR spectroscopy, which showed a signal at 4.05 ppm corresponding to the ethylenic hydrogen. In fact a pair of signals was obtained because this structure could be either *cis* or *trans*. A number of  $^{13}\text{C}$  NMR signals were observed in the region around 200 ppm. This suggests that either the ketone did not completely react or that an equilibrium exists between the starting material and the aldol product.

- Reduction of benzophenone with  $\text{Me}_2\text{HSiOTf}$  in chloroform.

Reaction of benzophenone with  $\text{Me}_2\text{HSiOTf}$  in chloroform at room temperature gives the fully reduced product  $\text{Ph}_2\text{CH}_2$ . Since ketones are more difficult to reduce, the reaction was carried out using two equivalents of  $\text{Me}_2\text{HSiOTf}$ . The  $^{13}\text{C}$  NMR spectrum showed that the signal arising from the  $\text{C}=\text{O}$  at 196 ppm disappeared to give a new signal at 43 ppm corresponding of the  $\text{CH}_2$  carbon of the alkane. Also a new signal appeared in the  $^1\text{H}$  NMR spectrum at 3.82 ppm corresponding to the  $\text{CH}_2$  of the alkane. We did not observe intermediates in this reaction.



**Scheme 20**

The mechanism suggests the attack of the oxygen of the benzophenone at the silicon atom, followed by hydrogen transfer to give the silyl ether. Exchange with  $\text{Me}_2\text{SiHOTf}$  from the silicon to the carbon atom of the alkoxy silane gives the diphenylmethane as final product.

- Conclusions for the reaction of ketones with  $\text{Me}_2\text{HSiOTf}$  in chloroform.

The reduction of ketones with  $\text{Me}_2\text{HSiOTf}$  is less efficient than the aldehydes reductions; the reaction has to be left longer at room temperature and two equivalents of  $\text{Me}_2\text{HSiOTf}$  are required in order to get a high yield.

With acetophenone and cyclohexanone, enolisation is observed which gives the corresponding aldol. Only ketones with no  $\alpha$ -hydrogens, such as benzophenone, could be reduced to the corresponding alkane. These reactions were repeated in the presence of salts.

2.10.2-Reduction of ketones with  $\text{Me}_2\text{HSiOTf}$  in the presence of  $\text{Bu}_4\text{N}^+\text{Y}^-$  ( $\text{Y}^- = \text{OTf}^-, \text{Cl}^-, \text{Br}^-$ ) in chloroform.

- Reduction of ketones with  $\text{Me}_2\text{HSiOTf}$  in the presence of  $\text{Bu}_4\text{N}^+\text{OTf}^-$ .

The reaction between ketones and two equivalents of  $\text{Me}_2\text{HSiOTf}$  in the presence of a triflate salt are comparable with those performed without the salt for the two enolisable ketones. Acetophenone and cyclohexanone both gave the aldol product but again the reaction does not go to completion since some of the ketone was present in the reaction mixture at the end of the reaction. Even if the reaction was left for a long time the ketones were not consumed.

However, benzophenone gave a different reduction product with the triflate salt, both the alcohol and ether were obtained from this reaction after hydrolysis.

The reduction of  $\text{Ph}_2\text{CO}$  is slow and the yield of ether,  $(\text{Ph})_2\text{CH-O-CH}(\text{Ph})_2$ , is very low (23 %).  $^1\text{H}$  NMR shows the appearance of new signal in the region of



7-7.5 ppm and a signal at 4.73 ppm corresponding to the hydrogen of the carbon near the oxygen of the ether.

- Reduction of ketones with  $\text{Me}_2\text{HSiOTf}$  in the presence of  $\text{Bu}_4\text{N}^+\text{Y}^-$  ( $\text{Y}^- = \text{Br}^-, \text{Cl}^-$ ).

Using other salts did not substantially change the outcome of the reaction, only the yields. The reduction of the benzophenone in the presence of other salts is not very efficient and even worse than with triflate salts. In fact, the yield of reduced product was never greater than 10 %.

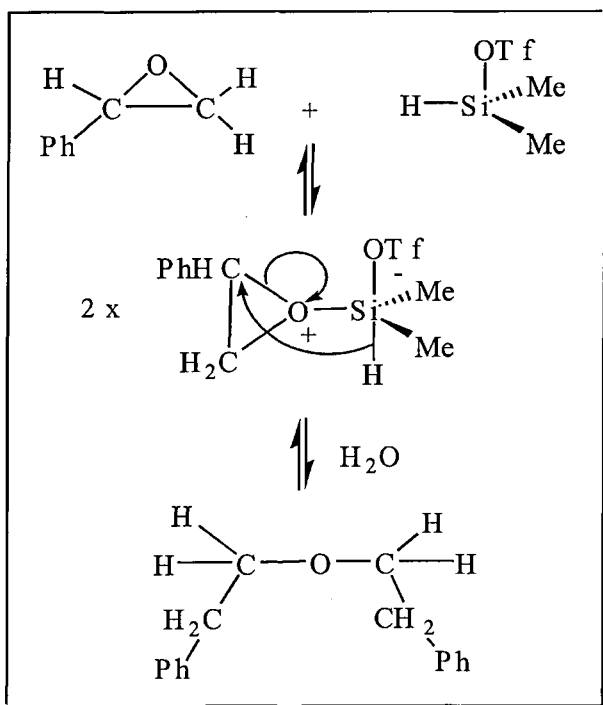
### **2.11-Reduction of styrene oxide with $\text{Me}_2\text{HSiOTf}$ or $\text{Me}_2\text{HSiCl}$ in chloroform.**

#### **2.11.1- Reduction with $\text{Me}_2\text{HSiOTf}$ in chloroform.**

We also examined the reaction between silanes and styrene oxide. Here we found that styrene oxide is also reduced by  $\text{Me}_2\text{HSiOTf}$  to give the corresponding ether.

The  $^{13}\text{C}$  NMR spectra of the reaction mixture showed that the signal at 52.3 ppm, corresponding to the CH ring of the styrene oxide, disappeared and gave a signal at 64.77 ppm, corresponding to the  $\text{CH}_2\text{O}$  of the ether  $(\text{PhCH}_2\text{CH}_2)_2\text{O}$ .

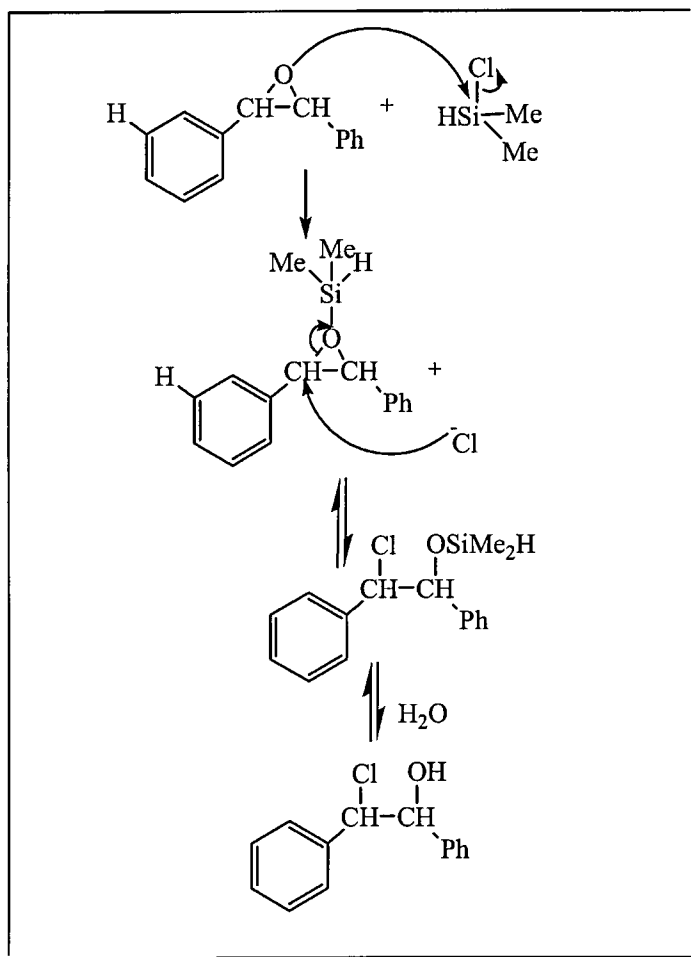
The  $^{13}\text{C}$  NMR spectroscopy data clearly proved formation of the ether but there was insufficient product to separate the ether from the mixture and isolate by distillation. Only one regioisomer was observed, presumably because the phenyl group stabilises the positive charge build up on the adjacent carbon in the activated complex of hydride transfer. The reaction is illustrated in Scheme 21.



**Scheme 21: Reduction of epoxide**

#### 2.11-2-Reduction with $\text{Me}_2\text{HSiCl}$ in chloroform.

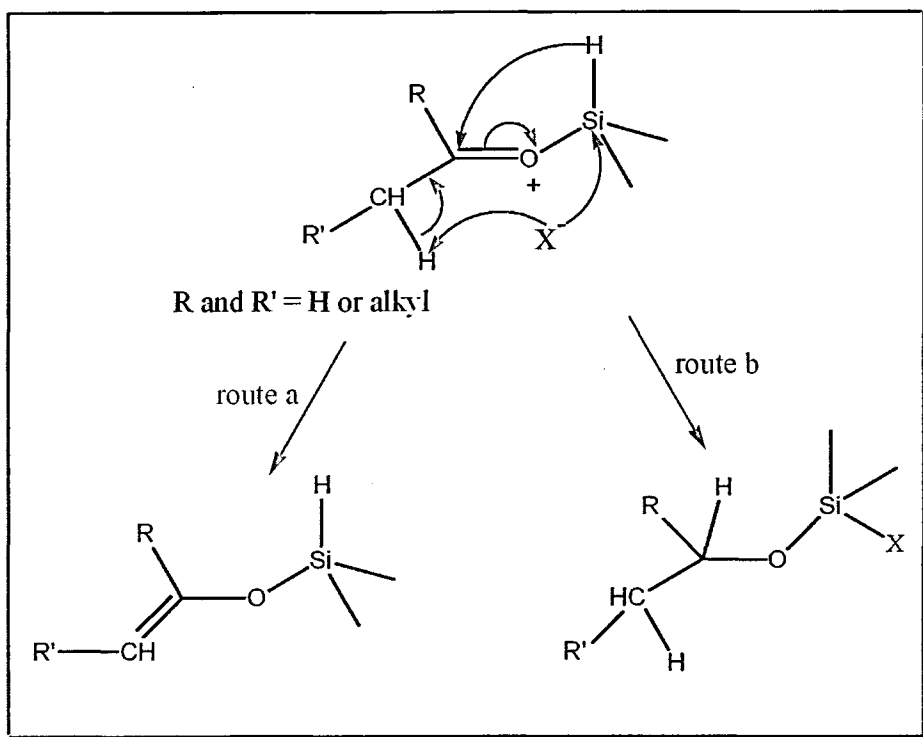
As with the aldehydes and ketones, the reduction was performed with another silane,  $\text{Me}_2\text{HSiCl}$ . Contrary to the reaction observed with  $\text{Me}_2\text{HSiOTf}$ , reduction did not occur but we observed an addition reaction. After silylation of the oxygen, the chloride ion attacks the carbon of the epoxide ring to give  $\text{PhCH}(\text{Cl})\text{-CH}_2\text{OH}$  or  $\text{PhCH}(\text{OH})\text{-CH}_2(\text{Cl})$  after hydrolysis. This reaction is illustrated in Scheme 22.



**Scheme 22: Reduction of styrene oxide with  $\text{Me}_2\text{HSiCl}$**

### 2.11.3-Conclusions.

The reduction of carbonyls with  $\text{Me}_2\text{HSiX}$ , where  $\text{X} = \text{OTf}$  or  $\text{Cl}$  in the presence of tetrabutylammonium salts or Amberlyst polymer occurred in moderate yield in the case of aldehydes. The yield of the reduction depends on the nature of the aldehyde. The reduction of ketones does not occur readily giving instead an aldol reaction. This is outlined in Scheme 23:



**Scheme 23:**Reduction of carbonyl group *via* aldol reaction ( route a) or hydrogen transfer ( route b).

Route b is predominant in the reduction of aldehydes, but route a is predominant in the reduction of ketones.

It is unlikely that proton abstraction, seen in route a, will be any different with aldehydes or ketones, so the reaction route b must be fast when using an aldehyde and slow when using a ketone. Nucleophiles react more slowly with ketones than aldehydes due to steric effect inhibition by the presence of an extra alkyl group in the ketone. Thus, with aldehydes proton transfer occurs easily and faster than proton abstraction from CH<sub>2</sub> to give the aldol product.

With ketones steric hindrance means that proton transfer occurs slowly and proton abstraction from CH<sub>2</sub> occurs predominantly giving the aldol product.

With benzophenone there are no  $\alpha$ -hydrogen atoms, so no proton abstraction can occur; reduction of benzophenone is the only route.

## 2.12-Experimental

The silanes used, especially those with a good leaving group, are moisture sensitive. In order to eliminate contamination by moisture, all the chemicals and reaction mixtures were treated as moisture sensitive compounds and handled under dry nitrogen. All chemicals employed in this study were purified by distillation. The pressure was adjusted to perform the distillation at a temperature between 50 and 150 °C. All chemicals were stored over molecular sieves under nitrogen prior to use.

All the NMR spectra were obtained using a Jeol JNM-LA300 spectrometer at 300 MHz for  $^1\text{H}$  NMR spectroscopy and 75 MHz for  $^{13}\text{C}$  NMR spectroscopy. A JEOL EX400 FT NMR spectrometer at 79.3 MHz was used for the acquisition of  $^{29}\text{Si}$  NMR. All studies of the reaction mixtures were performed in solution in deuteriochloroform and chemical shifts ( $\delta$ ) are quoted in parts per million (ppm) from tetramethylsilane (TMS) as a reference. Coupling constants  $J$  are in Hz and the multiplicity of the signal is s-singlet, d-doublet, t-triplet, q-quartet and m-multiplet.

FTIR spectra were carried out using a Perkin-Elmer 1710 infra-red Fourier transform spectrometer or using a Nicolet 205 FT-IR using NaCl plates.

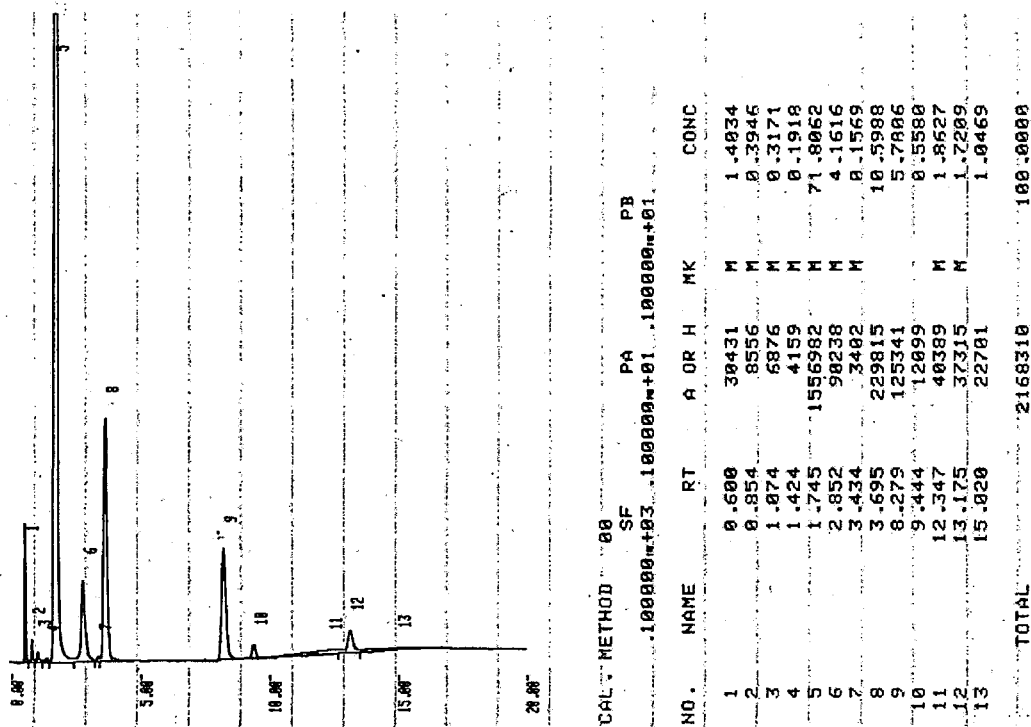
Melting points were obtained on an Electrothermal Digital melting point apparatus.

The gas chromatography was performed on a Perkin Elmer Gas Chromatograph equipped with a methyl silicon bonded capillary column (25 m, 5  $\mu$  film thickness, 0.53 mm i.d.) and using a flame ionisation detector. A mixture of hydrogen/air was used as carrier gas.

**Calculation of yield by GC.**

The calculation of yield by gas chromatography will be explained using the reaction of the benzaldehyde with dimethylbutoxysilane in the presence of tetrabutylammonium chloride as an example. This example was reported in detail in Section 2.8.2.

In this case the analysis by gas chromatography was performed twice, see Figures below, one corresponding to the beginning of the reaction (initial time) and one corresponding to an overnight reaction (final time).



**Figure 8: Chromatogram at the beginning of the reaction of the benzaldehyde with dimethylbutoxysilane in the presence of tetrabutylammonium chloride.**

In Figure 8, we see four important signals:

- dimethylbutoxysilane: the signal assigned 6, with a retention time equal to 2.85 min and a relative signal area equal to 4.16

- standard o-xylene: the signal assigned 8, with a retention time equal to 3.7 min and a relative signal area equal to 10.6
- benzaldehyde: the signal assigned 9, with a retention time equal to 8.28 min and a relative signal area equal to 5.78
- benzyl butyl ether: the signal assigned 10, with a retention time equal to 9.44 min and a relative signal area equal to 0.55

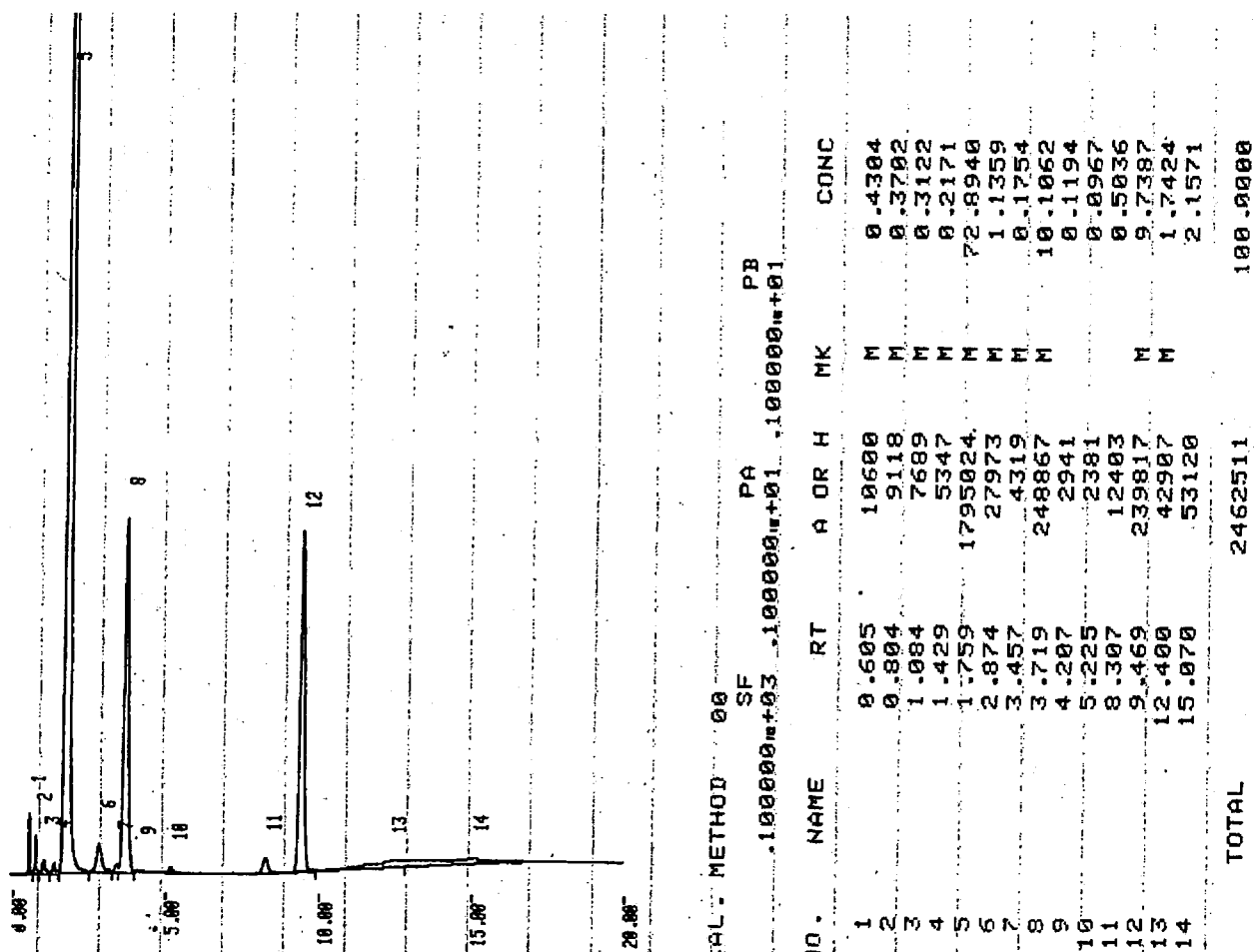


Figure 9: Chromatogram after overnight reaction of the benzaldehyde with dimethylbutoxysilane in the presence of tetrabutylammonium chloride.

In Figure 9, we see the same four important signals but in different proportions:

- dimethylbutoxysilane: the signal assigned 6, with a retention time equal to 2.87 min and a relative signal area equal to 1.13
- standard o-xylene: the signal assigned 8, with a retention time equal to 3.72 min and a relative signal area equal to 10.11
- benzaldehyde: the signal assigned 11, with a retention time equal to 8.3 min and a relative signal area equal to 0.5
- benzyl butyl ether: the signal assigned 12, with a retention time equal to 9.47 min and a relative signal area equal to 9.74.

In order to obtain the concentration of the different reagents and products, all the signal areas of the reagent or product are divided by the signal area of the standard. This gave the signal area ratio which avoids errors arising from, for example, the amount of mixture injected by the syringe into the gas chromatograph.

$$[\text{signal area ratio}] = [\text{signal area reagent or product}] / [\text{signal area of standard}]$$

The signal area ratio can be used to determine concentrations in g/l. First, the gas chromatography column is calibrated for all the reagents and products. The calibration is achieved by injecting onto the gas chromatograph a known amount of reagent and standard. This gave a signal area ratio for the reagents and the standard. If this is repeated with mixtures with known but different relative amount of reagent and standard, a graph of signal area ratio against mass ratio can be drawn, as shown in Graph 7 and 8. The gradient can then be calculated for each compound and can be used to calculate the unknown

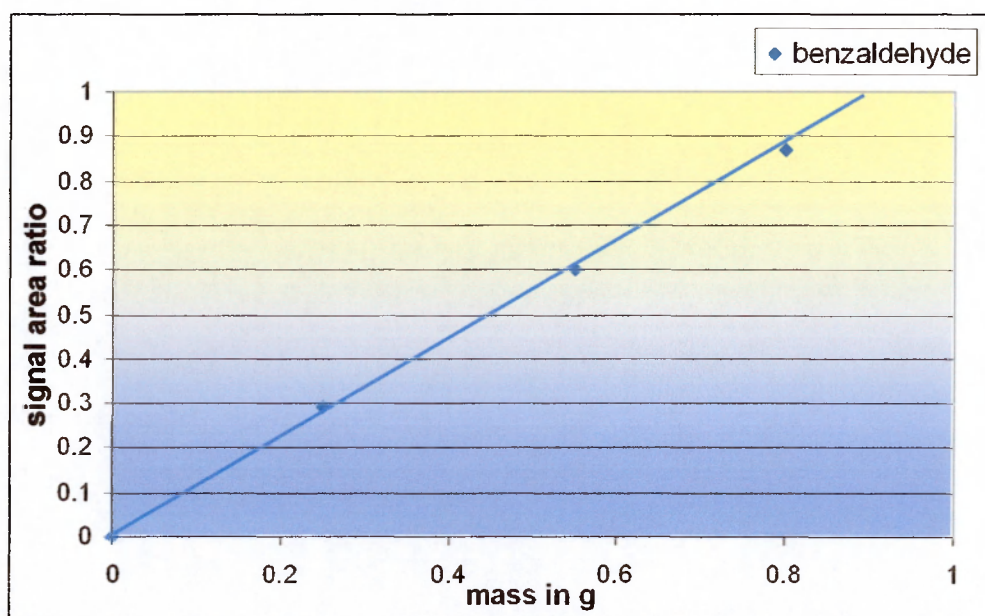


concentration of reagent for any signal area ratio obtained experimentally, providing the amount of standard is known.

Calibration of the response factor for benzaldehyde:

Mass sample in g	Mass standard in g	signal area standard	signal area benzaldehyde	signal area ratio
0	0	0	0	0
0.25	0.530	11.3	3.32	0.290
0.55	0.530	10.5	6.32	0.600
0.8	0.530	10.2	8.92	0.870

**Table 7: Calculation of mass ratio and signal area ratio**

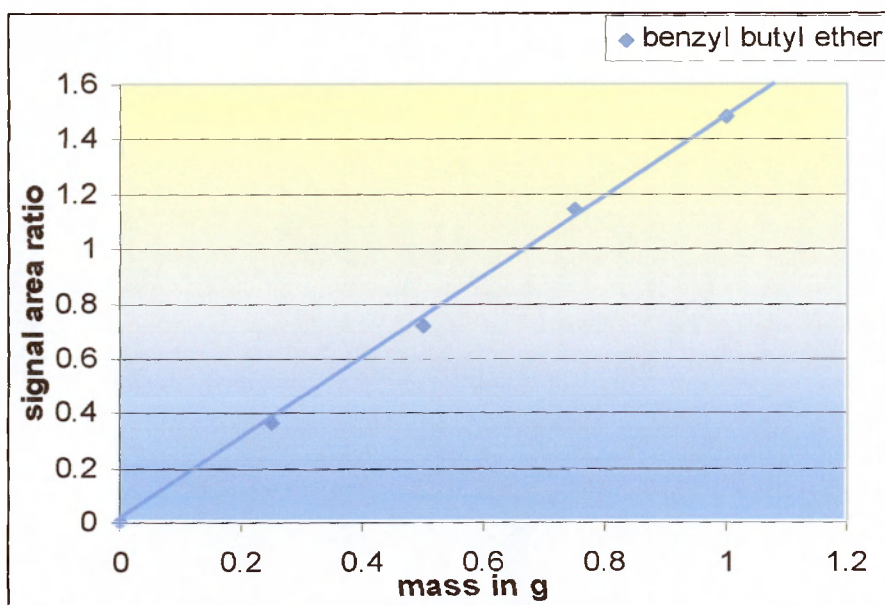


**Graph 7: Graph of signal area ratio against mass for benzaldehyde.**

Calibration of the response factor for benzyl butyl ether:

Mass sample in g	Mass standard in g	signal area standard	signal area benzyl butyl ether	signal area ratio
0	0	0	0	0
0.25g	0.530	10.9	2.01	0.360
0.5	0.530	10.3	3.80	0.720
0.75	0.530	10.1	5.74	1.14
1	0.530	9.83	7.29	1.48

**Table 8: Calibration of the response factor for benzyl butyl ether**



**Graph 8: Graph of signal area ratio against mass.**

So, for benzaldehyde response factor is the gradient of Graph 7 equal to 1.09 and for benzyl butyl ether response factor is the gradient of Graph 8 equal to 1.48. To calculate the amount of unknown compound we use the equation:

$$\text{Amount compound} = (\text{signal ratio} / \text{response factor}) \times \text{amount of standard}$$

So in these examples the yield is:

$$\text{Yield in reagents \%} = [(\text{amount of compound}) / (\text{initial amount of compound})] \times 100$$

$$\text{Yield of product obtained in \%} = [(\text{amount of compound}) / (\text{theoretical yield of compound})] \times 100$$

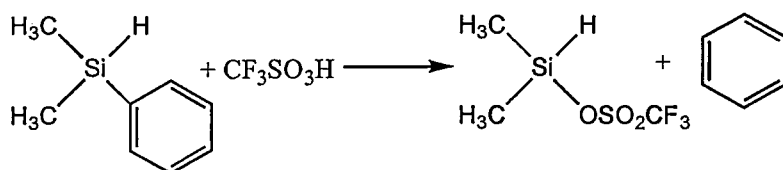
The theoretical yield of compound is worked out on molar basis from stoichiometry of the equation and knowing the quantity of reactants. The error in yields comes from the error in measuring the peak area by the instrument and the error involved in making up the solution. The main error is the measurement of the peak area as the solution is made up by mass so the error in

this case is low. The measurement error was calculated by doing repeated injections and determining the standard deviation in the peak area. In our experiments the error is 5 %.

## 2.12.1-Reduction of aldehyde with Me<sub>2</sub>HSiOTf

### 2.12.1.1-Synthesis of silanes.

All silanes employed were extremely moisture sensitive. All synthesis were carried out in sealed systems under an inert atmosphere of nitrogen.



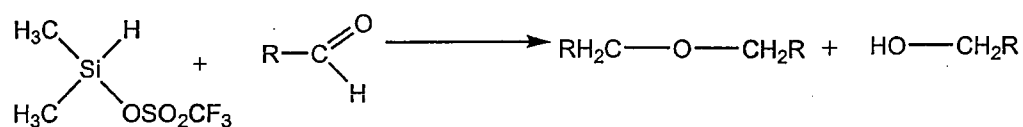
Synthesis of dimethylsilyl triflate: Dimethylsilyl triflate can be synthesised by the reaction of trifluoromethanesulfonic acid (triflic acid, HSO<sub>3</sub>CF<sub>3</sub>) with phenyldimethylsilane.

Stoichiometric quantities of triflic acid (50 g; 0.33 mol) were added to phenyldimethylsilane (44.97 g; 0.33 mol) in chloroform, with stirring at 0 °C (ice bath) under an atmosphere of dry nitrogen. <sup>1</sup>H NMR spectroscopy was used to follow the reaction to indicate the formation of the silyltriflate. The product was purified by distillation. Yield: 52.5 g; 76 % (Bp 125 °C / 760 mmHg)

NMR (δ, ppm): δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.6 (1H, m, <sup>3</sup>J = 3 Hz, Si-H); 0.4 (Me<sub>2</sub>-Si, d, <sup>3</sup>J = 3 Hz, 6H); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 118.30 (q, J<sub>CF</sub> = 324 Hz, CF<sub>3</sub>); -1.55 (Me-Si); <sup>29</sup>Si (79.3 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si): 24.5

NMR spectroscopy data were identical to the literature values <sup>42, 43</sup>.

#### 2.12.1.2-Reactions of aldehydes with Me<sub>2</sub>HSiOTf in chloroform.

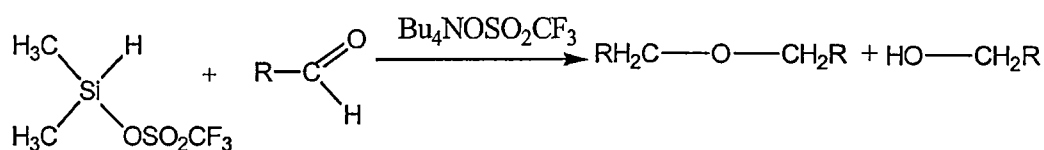


Benzaldehyde (0.5 g, 4.7 mmol) in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature and 1 mole equivalent of Me<sub>2</sub>HSiOTf (0.98 g, 4.7 mmol) was added to the solution. The mixture was stirred overnight. Water (10 ml) was added and the mixture was extracted with diethyl ether (2×10 ml). The organic phase was dried with magnesium sulfate and the solvent removed under reduced pressure.

The mixture was analysed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

**Product:** complex mixture δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.46 (6H, s, SiMe<sub>2</sub>), 3.44 (2H, s, CH<sub>2</sub>) and 7.11-8.2 (5H, m, aromatic); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.2 (SiMe<sub>2</sub>), 35.8 (t, CH<sub>2</sub>), 39.3 (t, CH<sub>2</sub>), 41.9 (t, CH<sub>2</sub>), 70.6 (CO), 120.4, 133.7, 134.44 and 138.2 .

#### 2.12.2-Reduction of aldehydes with Me<sub>2</sub>HSiOTf in chloroform in the presence of Bu<sub>4</sub>NOTf.



Aldehyde (4.7 mmol) in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature, and 2 mole equivalents of Me<sub>2</sub>HSiOTf (9.4 mmol), were added to the solution followed by just over 1 mole equivalent of tetrabutylammonium triflate (5.8 mmol). The mixture was stirred overnight. Water (10 ml) was added and the mixture was extracted with diethyl ether (2×10 ml). The organic phase was dried with magnesium sulfate and the solvent removed under reduced pressure.

#### 2.12.2.1 Reduction of benzaldehyde.

The NMR spectroscopy data were identical to literature values for the ether <sup>44</sup>; yield = 80 %

time (min)	concentration in g/l		
	benzaldehyde	dibenzyl ether	benzyl alcohol
0	25	0	2.10
720	2.04	19.6	0.750
Yield in %	8	80	3

**Table 9: Concentration in g/l of reagents and product with time.**

#### 2.12.2.2-Reduction of Octanal.

The NMR spectroscopy data were identical to the literature values<sup>45</sup>; yield = 66 %

time (min)	concentration in g/l		
	Octanal	dioctyl ether	octanol
0	25.3	0	3.01
720	5.58	16.1	2.49
Yield in %	22	66	10

**Table 10: Concentration in g/l of reagents and product with time.**

#### 2.12.2.3-Reduction of trimethylacetaldehyde.

The NMR spectroscopy data were identical to literature value<sup>46</sup>; yield = 47 %.

time (min)	concentration in g/l	
	Trimethyl-acetaldehyde	bis-(2,2-dimethylpropyl) ether
0	24.9	0
720	7.68	11.5
Yield in %	31	47

**Table 11: Concentration in g/l of reagents and product with time**

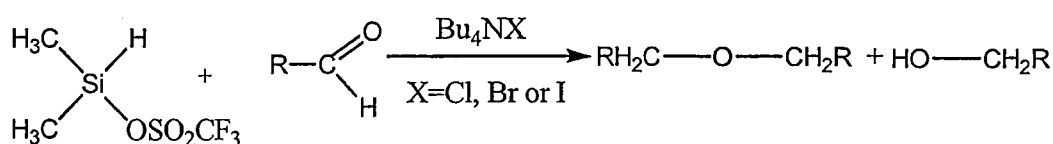
#### 2.12.2.4-Reduction of 2-methylbutanal.

The NMR spectroscopy data were identical to literature values<sup>47, 48</sup>; yield = 44 %.

time (min)	concentration in g/l	
	2-methylbutanal	bis-(2-methylbutyl) ether
0	25.1	0
720	9	10.2
Yield in %	36	44

**Table 12: Concentration in g/l of reagents and product with the time**

2.12.3-Reduction of aldehydes with Me<sub>2</sub>HSiOTf in chloroform in the presence of Bu<sub>4</sub>NBr, Cl, I.



Aldehyde (4.7 mmol) in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature and 2 mole equivalents of  $\text{Me}_2\text{HSiOTf}$  (9.4 mmol) were added to the solution. The tetrabutylammonium salts (1 mole equivalent) were then added, separately, and the mixture stirred overnight. Water (10 ml) was added and the mixture was extracted with diethyl ether (2×10 ml). The organic phase was dried with magnesium sulfate and the solvent removed under reduced pressure.

#### 2.12.3.1-Reduction of benzaldehyde.

A- Addition of tetrabutylammonium chloride: Yield of dibenzyl ether is 67 %

B-Addition of tetrabutylammonium bromide: Yield of dibenzyl ether is 43 %

C-Addition of tetrabutylammonium iodide: Yield of dibenzyl ether is 43 %.

time (min)	<b>Bu<sub>4</sub>NCl</b>		<b>Bu<sub>4</sub>NBr</b>		<b>Bu<sub>4</sub>NI</b>	
	benzaldehyde	dibenzyl ether	benzaldehyde	dibenzyl ether	benzaldehyde	dibenzyl ether
0	25.1	0	25.0	0	25.1	0
720	5.08	16.2	7.25	10	8.75	10.0
Yield in %	20	67	29	43	35	43

**Table 13: Yields in % and concentration in g/l of the reagents and products with time using different salts.**

#### 2.12.3.2-Reduction of octanal

A- Addition of tetrabutylammonium chloride: Yield of dioctyl ether is 54 %

B-Addition of tetrabutylammonium bromide: Yield of dioctyl ether is 48 %

C-Addition of tetrabutylammonium iodide: Yield of dioctyl ether is 40 %.

time (min)	Bu <sub>4</sub> NCl		Bu <sub>4</sub> NBr		Bu <sub>4</sub> NI	
	octanal	dioctyl ether	Concentration in g/l		octanal	dioctyl ether
			octanal	dioctyl ether		
0	25.0	0	25.1	0	25	0
720	7.26	13	8.81	12.6	1.13	9.49
Yield in %	29	54	35	48	44	40

**Table 14: Yields in % and concentration in g/l of the reagents and products with time using different salts.**

#### 2.12.3.3-Reduction of trimethylacetaldehyde.

A- Addition of tetrabutylammonium chloride: Yield of bis-(2,2-dimethylpropyl) ether is 31 %

B-Addition of tetrabutylammonium bromide: Yield of bis-(2,2-dimethylpropyl) ether is 25 %

C-Addition of tetrabutylammonium iodide: Yield of bis-(2,2-dimethylpropyl) ether is 12 %.

time (min)	Bu <sub>4</sub> NCl		Bu <sub>4</sub> NBr		Bu <sub>4</sub> NI	
	trimethyl-acetaldehyde	bis-(2,2-dimethyl propyl) ether	Concentration in g/l		trimethyl-acetaldehyde	bis-(2,2-dimethyl propyl) ether
			trimethyl-acetaldehyde	bis-(2,2-dimethyl propyl) ether		
0	25.1	0	25.1	0	25.0	0
720	12.6	7.21	15.6	6.95	17.3	6.25
Yield in %	50	31	62	25	69	12

**Table 15: Yields in % and concentration in g/l of the reagents and products with time using different salts.**

#### 2.12.3.4-Reduction of 2-methylbutanal.

A- Addition of tetrabutylammonium chloride: Yield of bis-(2-methylbutyl) ether is 33 %



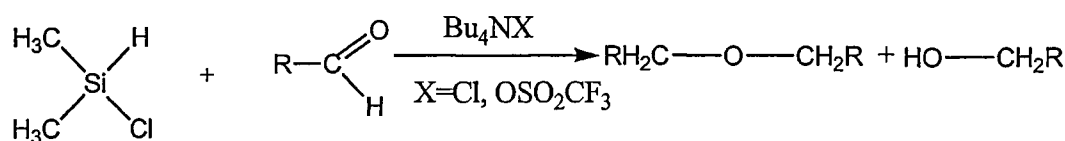
B-Addition of tetrabutylammonium bromide: Yield of bis-(2-methylbutyl) ether is 27 %

C-Addition of tetrabutylammonium iodide: Yield of bis-(2-methylbutyl) ether is 17 %.

time (min)	Bu <sub>4</sub> NCl		Bu <sub>4</sub> NBr		Bu <sub>4</sub> NI	
	2-methyl butanal	bis-(2- methylbutyl) ether	2-methyl butanal	bis-(2- methylbutyl) ether	2-methyl butanal	bis-(2- methylbutyl) ether
0	25	0	25.0	0	25.0	0
720	11.5	7.63	14.8	6.40	16	4.10
Yield in %	46	33	59	27	64	17

**Table 16: Yields in % and concentration in g/l of the reagents and products during the time using different salts.**

#### 2.12.4-Reduction of aldehydes with Me<sub>2</sub>HSiCl in the presence of Bu<sub>4</sub>NOTf or Bu<sub>4</sub>NCl.



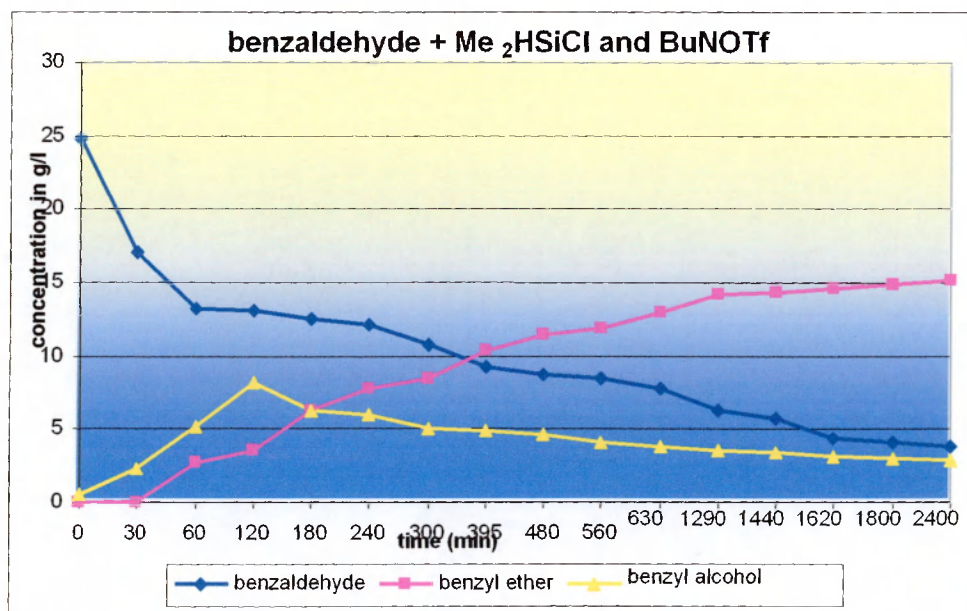
Aldehyde (4.7 mmol) in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature and 2 mole equivalents of Me<sub>2</sub>HSiCl (9.4mmol) were added to the solution followed by either 1 mole equivalent of tetrabutylammonium triflate (4.7 mmol) or 1 mole equivalent of tetrabutylammonium chloride (4.7 mmol). The mixture was stirred overnight. Water (10 ml) was added and the mixture was extracted with diethyl ether (2×10 ml). The organic phase was dried with magnesium sulfate and the solvent removed under reduced pressure.

#### 2.12.4.1- Reduction of benzaldehyde.

The results are shown in Table 17. Yields of dibenzyl ether are 69 % when using tetrabutylammonium triflate and 46 % when using tetrabutylammonium chloride.

time (min)	concentration in g/l		
	benzaldehyde	dibenzyl ether	benzyl alcohol
0	24.8	0	0.590
30	17.1	2.73	2.35
60	13.3	3.49	5.22
120	13.1	6.33	8.24
180	12.6	7.80	6.27
240	12.1	8.48	5.99
300	10.8	10.3	5.01
395	9.25	11.5	4.85
480	8.79	11.9	4.57
560	8.44	13.0	4.10
630	7.73	14.2	3.82
1290	6.33	14.3	3.60
1440	5.70	14.6	3.35
1620	4.34	14.7	3.20
1800	4.12	14.9	3.00
2400	3.86	15.1	2.81
yield in %	15.0	69.0	12.0

**Table 17: Yields in % and concentration in g/l of the reagents and products with time.**



**Graph 9: Concentration in g/l of the reagents and products followed over time.**

Benzaldehyde + Me<sub>2</sub>HSiCl and Bu<sub>4</sub>NCl:

time (min)	concentration in g/l		
	benzaldehyde	dibenzyl ether	benzyl alcohol
0	24.9	0	2.35
720	7.50	11.0	5.17
Yield in %	29	46	21

**Table 18: Yields in % and concentration in g/l of the reagents and products with time.**

#### 2.12.4.2-Reduction of butanal.

The yield of dibutyl ether was 58 % when Bu<sub>4</sub>NOTf was used and 35 % when Bu<sub>4</sub>NCl was used. The NMR spectroscopy data were identical to the literature values<sup>49</sup>.

Butanal + Me<sub>2</sub>HSiCl and Bu<sub>4</sub>NOTf:

time (min)	concentration in g/l		
	butanal	dibutyl ether	butyl alcohol
0	25.0	0	1.97
720	6.50	8.99	3.32
Yield in %	26	58	13

**Table 19: Yields in % and concentration in g/l of the reagents and products with time.**

Butanal + Me<sub>2</sub>HSiCl and Bu<sub>4</sub>N Cl:

time (min)	concentration in g/l		
	butanal	dibutyl ether	butyl alcohol
0	25.0	0	1.55
720	10.8	5.90	5.50
Yield in %	43	35	22

**Table 20: Yields in % and concentration in g/l of the reagents and products with time.**

2.12.4.3-Reduction of octanal.

The yield of dioctyl ether was 39 % when Bu<sub>4</sub>NOTf was used and 29 % when Bu<sub>4</sub>NCl was used.

Octanal + Me<sub>2</sub>HSiCl and Bu<sub>4</sub>N OTf:

time (min)	concentration in g/l		
	octanal	dioctyl ether	octanol
0	25.1	0	3.20
720	11.0	9.80	4.26
Yield in %	40	39	17

**Table 21: Yields in % and concentration in g/l of the reagents and products with time.**

Octanal + Me<sub>2</sub>HSiCl and <sup>t</sup>Bu<sub>4</sub>N Cl:

time (min)	concentration in g/l		
	octanal	dioctyl ether	octanol
0	25.1	0	2.78
720	11.9	7.28	5.74
Yield in %	47	29	23

**Table 22: Yields in % and concentration in g/l of the reagents and products with time.**

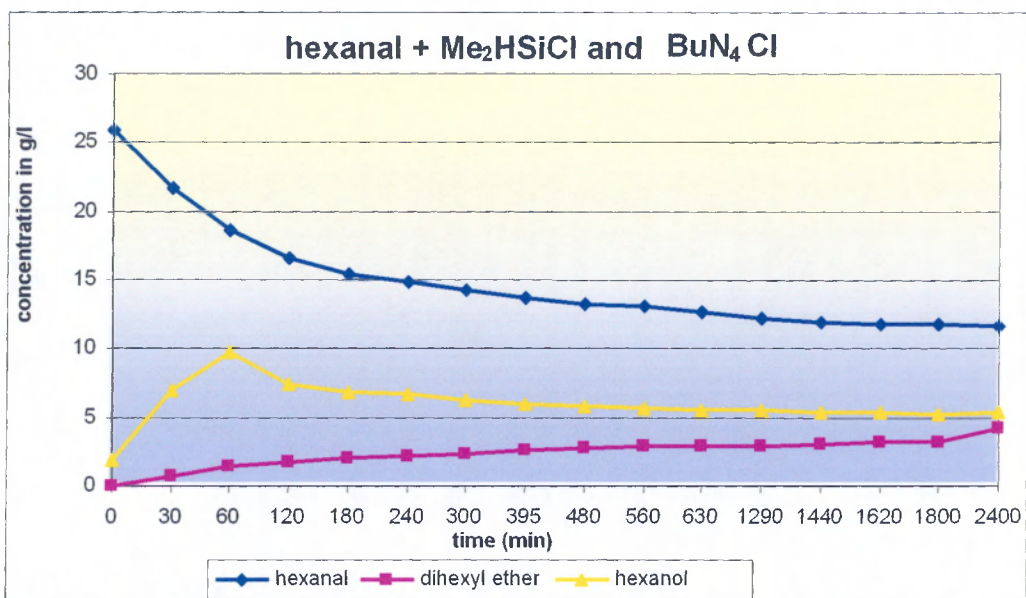
2.12.4.4-Reduction of hexanal

The yield of dihexyl ether was 43 % when Bu<sub>4</sub>NOTf was used and 25 % when Bu<sub>4</sub>NCl was used.

The results are shown in Table 23:

time (min)	concentration in g/l		
	Hexanal	dihexyl ether	hexanol
0	25.9	0	1.90
30	21.6	0.78	7.03
60	18.7	1.43	9.71
120	16.5	1.75	7.49
180	15.7	2.03	6.91
240	14.9	2.19	6.68
300	14.3	2.35	6.22
395	13.8	2.62	6.01
480	13.3	2.75	5.80
560	13.1	2.95	5.71
630	12.7	2.93	5.60
1290	12.2	2.97	5.53
1440	12	3.10	5.43
1620	11.9	3.20	5.38
1800	11.7	3.23	5.31
2400	11.7	4.24	5.40
yield in %	48	25	21

**Table 23: Yields in % and concentration in g/l of the reagents and products with time.**



Graph 10: Concentration in g/l of the reagents and products with time.

Hexanal +  $\text{Me}_2\text{HSiCl}$  and  $\text{Bu}_4\text{N OTf}$ :

time (min)	concentration in g/l		
	Hexanal	dihexyl ether	hexanol
0	25.3	0	2.28
720	8.60	10	4.27
Yield in %	34	43	17

Table 24: Yields in % and concentration in g/l of the reagents and products with time.

#### 2.12.4.5-Reduction of trimethylacetaldehyde.

The yield of bis-(2,2-dimethylpropyl) ether was 38 % when  $\text{Bu}_4\text{NOTf}$  was used and 22 % when  $\text{Bu}_4\text{NCl}$  was used.

Trimethylacetaldehyde +  $\text{Me}_2\text{HSiCl}$  and  $\text{Bu}_4\text{NOTf}$ :

time (min)	concentration in g/l	
	trimethyl-acetaldehyde	bis-(2,2-dimethylpropyl) ether
0	25.2	0
720	12.3	8.78
Yield in %	49	38

Table 25: Yields in % and concentration in g/l of the reagents and products with time.

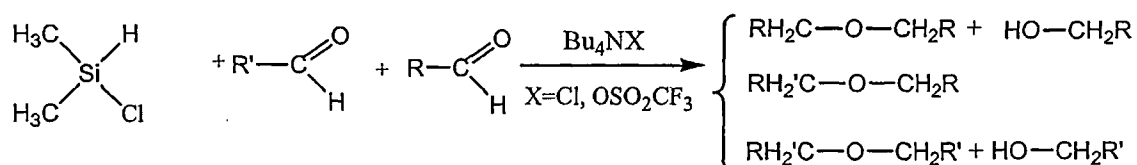
Trimethylacetaldehyde + Me<sub>2</sub>HSiCl and Bu<sub>4</sub>NCl:

time (min)	concentration in g/l	
	trimethyl-acetaldehyde	bis-(2,2-dimethylpropyl) ether
0	25.2	0
720	14.6	4.24
Yield in %	58	22

**Table 26: Yields in % and concentration in g/l of the reagents and products with time.**

2.12.5-Reduction of a mixture of two different aldehydes with

Me<sub>2</sub>HSiCl in the presence of nucleophiles in chloroform.



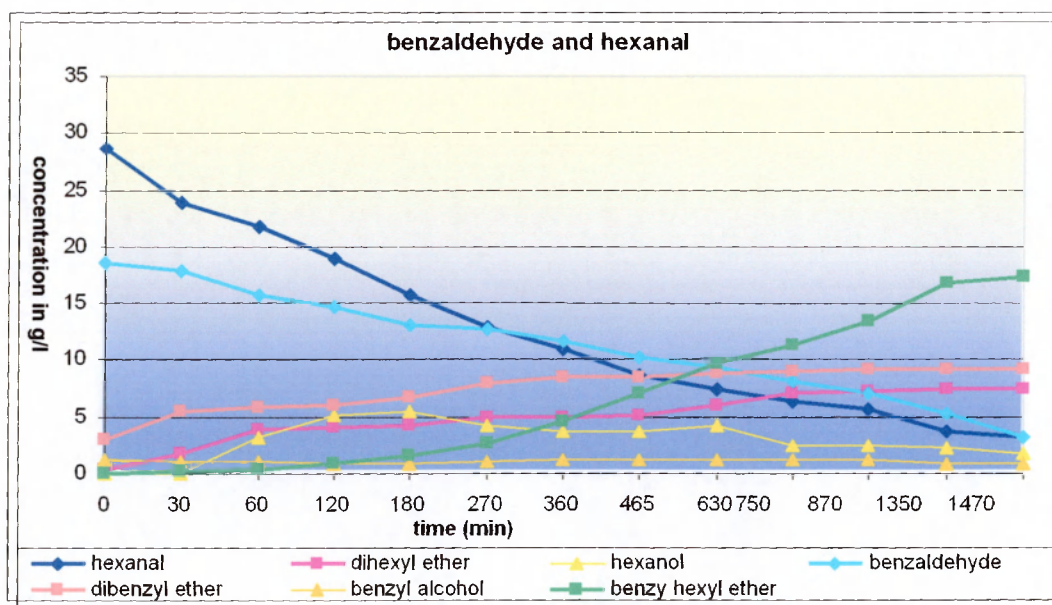
An aldehyde, RCHO, (4.7 mmol) and 1 equivalent of a second aldehyde, R'CHO, in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature and 2 mole equivalents of Me<sub>2</sub>HSiCl (2×10 mmol) were added to the solution, followed by 1 mole equivalent of tetrabutylammonium triflate (5 mmol). Water (10 ml) was added and the mixture was extracted with diethyl ether (2×10 ml). The organic phase was dried with magnesium sulfate and the solvent removed under reduced pressure.

2.12.5.1-Reduction of benzaldehyde and hexanal.

The results obtained with benzaldehyde (RCHO) and hexanal (R'CHO) are shown in Table 27 and Graph 11:

	hexanal	dihexyl ether	hexanol	benzaldehyde	dibenzyl ether	benzyl alcohol	benzyl hexyl ether
time (min)	concentration in g/l						
initial	26.3	0	0	25	0	1.88	0
0	28.6	0.320	0	18.6	3.07	1.16	0
30	23.9	1.76	0	17.9	5.50	1.01	0.130
60	21.8	3.96	3.20	15.8	5.76	1.01	0.270
120	18.9	4.03	5.17	14.8	6.07	0.870	0.810
180	15.8	4.21	5.41	13.0	6.70	0.870	1.61
270	12.9	4.88	4.18	12.8	7.90	1.01	2.69
360	11	5.03	3.69	11.6	8.44	1.16	4.58
465	8.70	5.12	3.69	10.3	8.51	1.16	7
630	7.40	6.07	4.18	9.40	8.87	1.30	9.70
750	6.30	7.11	2.46	8.06	8.94	1.30	11.32
870	5.60	7.26	2.46	7.12	9.11	1.16	13.47
1350	3.70	7.50	2.21	5.24	9.20	0.870	16.71
1470	3.10	7.44	1.77	3.13	9.25	0.870	17.25
yield in %	11	16	6	12	20	4	38

**Table 27: Yields in % and concentration in g/l of the reagents and products with time.**



**Graph 11: concentration in g/l of the reagents and products followed over time.**

**Dibenzyl ether:** Yield 21 %. The NMR spectroscopy data were identical to the literature values.

**Dihexyl ether:** Yield 16 %. The NMR spectroscopy data were identical to the literature values<sup>50</sup>.



**Benzyl hexyl ether:** Yield 39 %. The NMR spectroscopy data were identical to the literature values<sup>51</sup>.

The results shown in Table 28 were obtained when the experiment was repeated using a 5.4 mmol equivalent.

compound	hexanal	dihexyl ether	benzaldehyde	dibenzyl ether	benzyl hexyl ether
initial [compound] in g/l	27.4	0	28.7	0	0
final [compound] in g/l	4.07	7.09	5.1	8.21	13.81
yield %	15	13	18	15	27

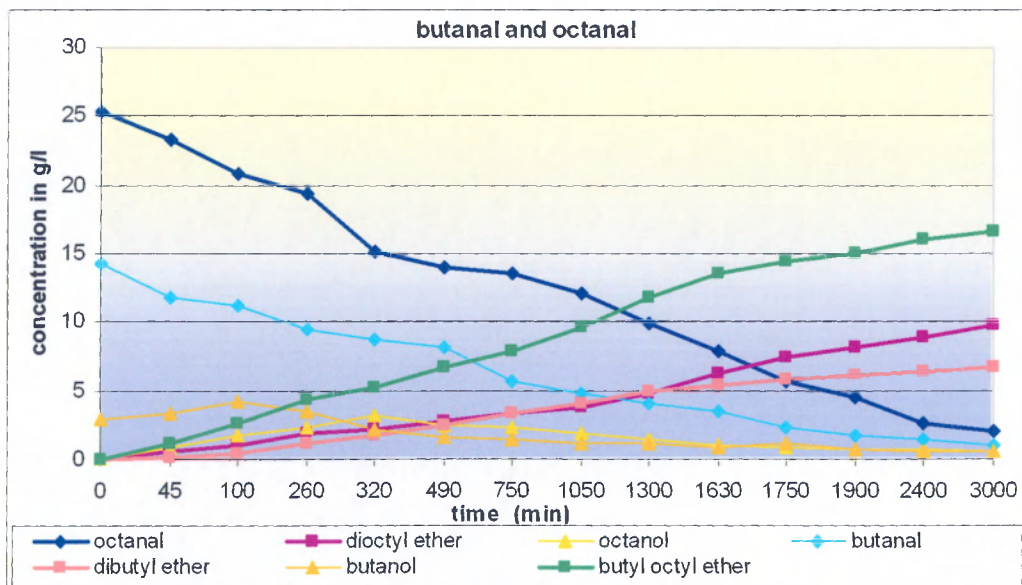
**Table 28: Yields in % and concentration in g/l of the reagents and products**

#### 2.12.5.2-Reduction of octanal and butanal.

The results obtained with octanal (RCHO) and butanal (R'CHO), when using tetrabutylammonium triflate are shown in Table 29 and Graph 12:

	octanal	octyl ether	octanol	butanal	butyl ether	butanol	butyl octyl ether
time (min)	concentration in g/l						
0	25.3	0	0	14.3	0	2.93	0
45	23.3	0.580	0.840	11.78	0.190	3.30	1.16
100	20.8	1.05	1.69	11.21	0.410	4.21	2.60
260	19.4	1.94	2.36	9.50	1.15	3.48	4.34
320	15.2	2.12	3.20	8.74	1.75	2.20	5.2
490	14	2.77	2.53	8.17	2.45	1.65	6.65
750	13.5	3.28	2.30	5.70	3.28	1.47	7.80
1050	12.1	3.85	1.86	4.75	4.15	1.10	9.54
1300	9.84	4.75	1.52	4.02	4.96	1.10	11.9
1630	7.87	6.32	1.01	3.51	5.42	0.910	13.6
1750	5.62	7.50	0.840	2.38	5.76	1.10	14.4
1900	4.49	8.12	0.670	1.71	6.13	0.730	15.0
2400	2.61	8.87	0.670	1.52	6.38	0.550	16.1
3000	2.03	9.74	0.510	1	6.77	0.550	16.6
yield in %	8	22	2	7	25	4	50

Table 29: Yields in % and concentration in g/l of the reagents and products over time.



Graph 12: Concentration in g/l of the reagents and products followed over time.

**Dioctyl ether:** Yield 21 %. The NMR spectroscopy data were identical to the literature values.

**Dibutyl ether:** Yield 24 %. The NMR spectroscopy data were identical to the literature values<sup>49</sup>.

**Butyl octyl ether:** Yield 49 %. The NMR spectroscopy data were identical to the literature values<sup>52</sup>.

#### 2.12.5.3-Reduction of benzaldehyde and butanal.

Results obtained with benzaldehyde (RCHO) and butanol (R'CHO), when using tetrabutylammonium triflate are shown in Table 30:

compound	benzaldehyde	dibenzyl ether	butanal	dibutyl ether	benzyl butyl ether
initial [compound] in g/l	24	0	17.1	0	0
final [compound] in g/l	2.6	4.51	2.28	6.37	17.9
yield %	11	21	12	20	43

**Table 30: Yields in % and concentration in g/l of the reagents and products over time.**

The NMR spectroscopy data were identical to the literature values<sup>53</sup>.

The result obtained when using tetrabutylammonium chloride are showed in Table 31.

compound	benzaldehyde	dibenzyl ether	butanal	dibutyl ether	benzyl butyl ether
initial [compound] in g/l	25	0	16.79	0	0
final [compound] in g/l	3.7	4.12	2.68	5	13.39
yield %	15	18	16	16	32

**Table 31: Yields in % and concentration in g/l of the reagents and products over time.**

#### 2.12.5.4-Reduction of benzaldehyde and trimethylacetaldehyde.

The results obtained with benzaldehyde (RCHO) and trimethylacetaldehyde (R'CHO), when using tetrabutylammonium triflate are shown in Table 32:

compound	benzaldehyde	dibenzyl ether	C(CH <sub>3</sub> ) <sub>3</sub> aldehyde	C(CH <sub>3</sub> ) <sub>3</sub> ether	benzyl-CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> ether
initial [compound] in g/l	24.5	0	20.2	0	0
final [compound] in g/l	3.81	9.49	3.76	5.15	25.34
yield %	16	20	19	16	35

**Table 32: Yields in % and concentration in g/l of the reagents and products over time.**

The NMR spectroscopy data were identical to the literature values<sup>54</sup>.

The results obtained when using tetrabutylammonium chloride are shown in

**Table 33:**

compound	benzaldehyde	dibenzyl ether	C(CH <sub>3</sub> ) <sub>3</sub> aldehyde	C(CH <sub>3</sub> ) <sub>3</sub> ether	benzyl-CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> ether
initial [compound] in g/l	24.9	0	20.3	0	0
final [compound] in g/l	4.64	7.91	4.48	4.35	17.32
yield %	19	16	22	13	26

**Table 33: Yields in % and concentration in g/l of the reagents and products over time.**

#### 2.12.5.5-Reduction of butanal and trimethylacetaldehyde.

The results obtained with butanal (RCHO) and trimethylacetaldehyde

(R'CHO), when using tetrabutylammonium triflate are shown in Table 34:

Compound	butanal	dibutyl ether	C(CH <sub>3</sub> ) <sub>3</sub> aldehyde	C(CH <sub>3</sub> ) <sub>3</sub> ether	butyl-CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> ether
Initial [compound] in g/l	23	0	23.5	0	0
Final [compound] in g/l	2.95	6.78	3.49	5.46	12.62
yield %	13	19	15	16	31

**Table 34: Yields in % and concentration in g/l of the reagents and products over time.**

The NMR spectroscopy data were identical to the literature value<sup>55</sup>.

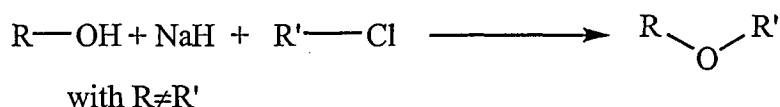
The results obtained when using tetrabutylammonium chloride are shown in

**Table 35:**

compound	butanal	dibutyl ether	C(CH <sub>3</sub> ) <sub>3</sub> aldehyde	C(CH <sub>3</sub> ) <sub>3</sub> ether	butyl-CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> ether
Initial [compound] in g/l	23	0	23.5	0	0
Final [compound] in g/l	4.84	5.43	5.1	4.32	7.86
yield %	20	15	22	12	21

**Table 35: Yields in % and concentration in g/l of the reagents and products over time.**

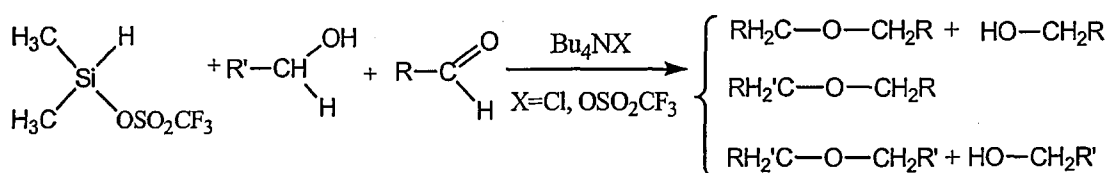
#### 2.12.5.6-Synthesis of mixed ether by Williamson's synthesis.



1 Mol of alcohol (ROH) was added to 1 mol equivalent of sodium hydride in THF and stirred for 1 h at room temperature. A solution of a 1 mol equivalent of alkyl chloride in THF was added dropwise to the mixture, which was then

stirred and refluxed for about 1 h. The mixture was cooled and analysed by GC and NMR spectroscopy. The NMR spectroscopy data were identical to the literature values<sup>56-59</sup>.

2.12.6-Reduction of aldehydes and alcohols together in the presence of  $\text{Me}_2\text{HSiX}$  and salt.



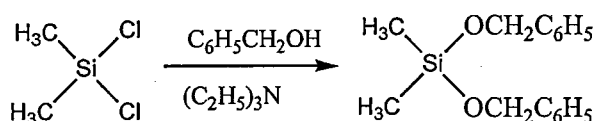
Butanal (0.7 g, 9.7 mmol) and octanol (1.3 g, 10 mmol) in a solution of chloroform (20 ml) were stirred under nitrogen at room temperature. 2 Mol equivalents of  $\text{Me}_2\text{HSiCl}$  (4.77 g; 19.4 mmol) were added to the solution together with 1 mol equivalent of tetrabutylammonium triflate (5.44 g, 10 mmol). The results are shown in Table 36:

Time (min)	concentration in g/l				
	octanol	butanal	dibutyl ether	butyl alcohol	butyl octyl ether
0	65.3	35.0	0.600	0.00	2.06
15	64.7	30.2	0.950	8.63	4.80
30	58.0	26.9	1.64	8.40	6.51
60	49.5	20.8	2.02	6.30	9.63
90	48.2	17.3	3.55	3.97	14.4
120	42.5	14.5	4.96	4.20	22.0
210	38.4	13.6	5.79	1.87	37.2
310	30.1	12.0	6.95	1.63	39.9
460	25.6	12.0	7.41	1.40	48.1
560	23.3	10.6	7.78	1.28	51.8
715	18.6	9.84	8.31	1.17	56.2
875	14.4	8.76	8.82	1.16	58.6
1470	6.43	8.13	9.92	1.05	62.3
1560	5.86	7.87	10.1	0.93	63.0

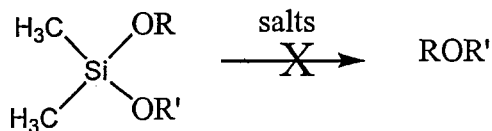
1695	5.04	6.86	10.5	0.900	62.6
1805	4.77	6.28	10.6	0.810	63.0
2100	3.91	5.95	11.0	0.700	63.3
yield in %	6.00	17.0	17.0	2.00	70

**Table 36: Yields in % and concentration in g/l of the reagents and products over time.**

#### 2.12.7-Reaction of dialkoxysilane with a nucleophilic salt.



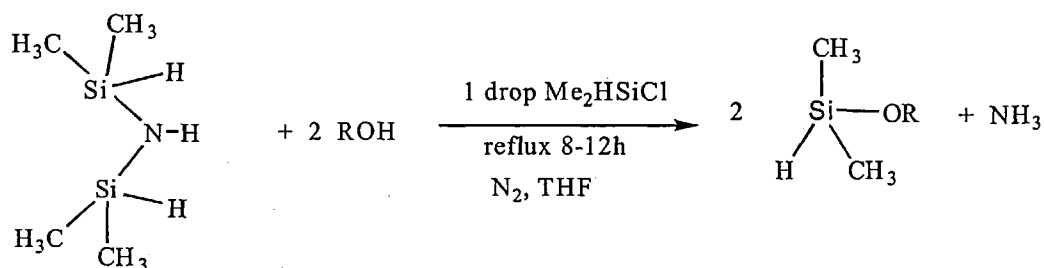
Dimethyldichlorosilane (2.05 g, 0.016 mol) was reacted with benzyl alcohol (1.73 g, 0.016 mol) in triethylamine (10 ml), at room temperature in a dry atmosphere of nitrogen. The mixture was stirred for about 1 h. The product was purified by distillation and characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy<sup>60</sup>.



No dialkylether was obtained, only starting material remained after reacting with tetrabutylammonium triflate

#### 2.12.8-Reduction of one aldehyde in the presence of an alkoxyhydrosilane.

#### 2.12.8.1-Synthesis of alkoxysilanes.



2 mol of the alcohol were mixed with 1 mol of tetramethyldisilazane in THF, under a dry atmosphere of nitrogen, at room temperature. One drop of dimethylchlorosilane was added and the mixture refluxed for 8 to 12 h.

Separation of the crude silyl ether,  $\text{Me}_2\text{HSiOR}$ , was achieved by distillation.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy permitted the characterisation of the product by comparison with the literature data<sup>61,62</sup>.

The aldehyde (4.7 mmol) and dimethylalkoxysilane (4.7 mmol) in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature with 2 mol equivalents of tetrabutylammonium chloride (1.31 g, 4.7 mmol). Water (10 ml) was added and the mixture was extracted with diethyl ether (2×10 ml). The organic phase was dried with magnesium sulfate and the solvent removed under reduced pressure.

#### 2.12.8.2-Reduction of benzaldehyde using dimethylbutoxysilane.

The results benzaldehyde using dimethylbutoxysilane are shown in Table 37:



Time (min)	concentration in g/l			
	benzaldehyde	benzyl alcohol	Butoxydimethylsilane	benzyl butyl ether
0	25.1	7.78	15.5	6
30	15.1	6.3	8.22	17.7
60	10.0	3.44	5.5	24.5
90	7.1	3.06	3.7	29.2
120	4.06	2.57	1.84	31.4
240	2.64	0.62	1.09	32.7
yield in %	10	2	7	85

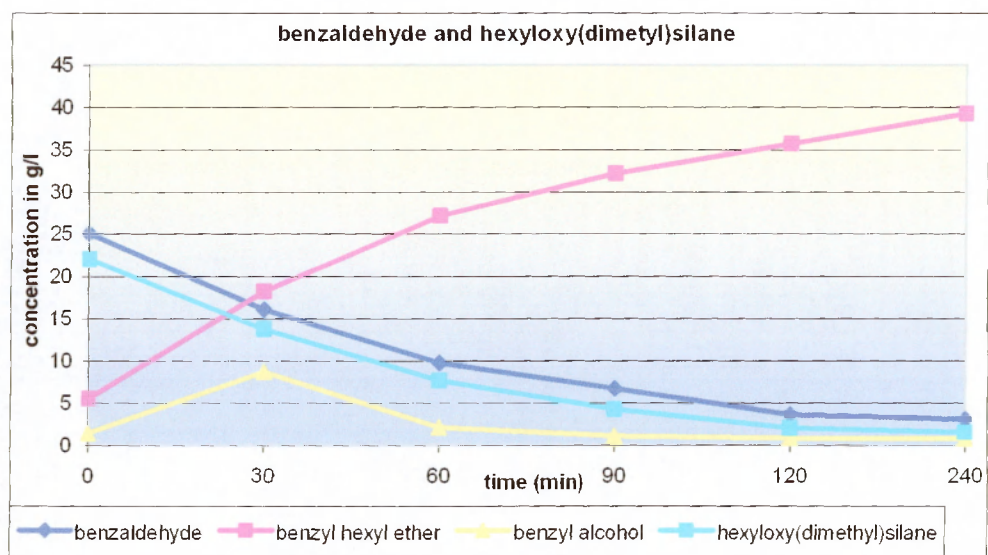
**Table 37: Yields in % and concentration in g/l of the reagents and products over time.**

#### 2.12.8.3-Reduction of benzaldehyde using dimethyl(hexyloxy)silane.

The reaction was repeated using benzaldehyde and dimethyl(hexyloxy)silane, and the results are shown in Table 38 and Graph 13:

Time (min)	benzaldehyde	benzyl alcohol	concentration in g/l	
			hexyloxy(dimethyl)silane	benzyl hexyl ether
0	25	1.40	22	5.47
30	16.03	8.62	13.7	18.2
60	9.72	2.06	7.65	27.1
90	6.67	1.08	4.20	32.2
120	3.59	0.850	2.04	35.7
240	3.05	0.780	1.53	39.3
yield in %	12	3	7	81

**Table 38: Yields in % and concentration in g/l of the reagents and products over time.**



**Graph 13: Concentration in g/l of the reagents and products over time.**

#### 2.12.8.4-Reduction of benzaldehyde with *tert*-butoxy(dimethyl)silane.

The results obtained using benzaldehyde with *tert*-butoxy(dimethyl)silane are shown in Table 39:

Time (min)	concentration in g/l			benzyl <i>tert</i> -butyl ether
	benzaldehyde	benzyl alcohol	<i>t</i> butoxy(dimethyl)silane	
0	25.6	5.02	22	6.60
240	4.99	2.50	1.97	39.0
<b>Yield in %</b>	<b>18</b>	<b>8</b>	<b>8</b>	<b>66</b>

**Table 39: Yields in % and concentration in g/l of the reagents and products over time.**

#### 2.12.8.5-Reduction of butanal with hexyloxy(dimethyl)silane.

The reaction was carried out as on p 90 using butanal (0.5 g, 5.81 mmol) and hexyloxy(dimethyl)silane (0.55 g, 2.9 mmol).

The results are shown in Table 40:

Time (min)	concentration in g/l			
	butanal	butanol	hexyloxy(dimethyl)silane	butyl hexyl ether
0	24.3	0.21	27.3	10.9
240	4.05	1.77	2.18	42
Yield in %	15	6	8	71

**Table 40:** Yields in % and concentration in g/l of the reagents and products over time.

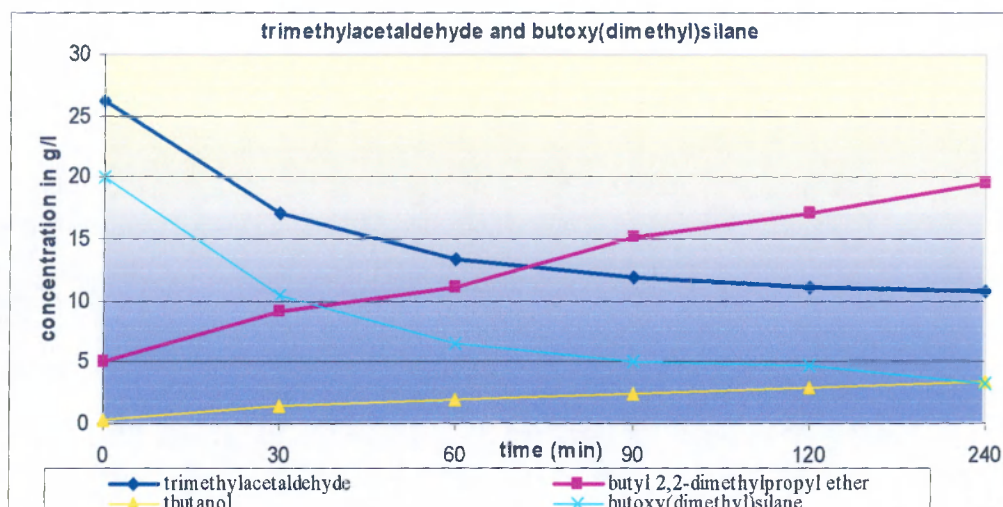
2.12.8.6-Reduction of trimethylacetaldehyde with butoxy(dimethyl)silane.

The reaction was carried out as on p 90 using trimethylacetaldehyde (0.52 g, 6 mmol) and dimethylbutoxysilane (0.4 g, 3 mmol)

The results are shown in Table 41 and Graph 14:

Time (min)	concentration in g/l			
	trimethylacetaldehyde	butyl alcohol	butoxy(dimethyl)silane	butyl 2,2-dimethylpropyl ether
0	26.3	0.29	20	5.03
30	17.1	1.54	10.5	9.09
60	13.3	1.88	6.56	11.2
90	11.9	2.39	5.08	15.2
120	11.1	2.90	4.67	17.2
240	10.7	3.36	3.25	19.5
yield in %	40	12	16	32

**Table 41:** Yields in % and concentration in g/l of the reagents and products over time.



**Graph 14: concentration in g/l of the reagents and products with time.**

2.12.9-Reduction of aldehydes with  $\text{Me}_2\text{HSiX}$  where  $\text{X} = \text{OTf}, \text{Cl}$  in chloroform in the presence of an Amberlyst resin.

The aldehyde (4.7 mmol) in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature. 2 Mol equivalents of  $\text{Me}_2\text{HSiOTf}$  (9.4 mmol) or  $\text{Me}_2\text{HSiCl}$  (9.4 mmol) were added to the solution, followed by 1 mol equivalent of the bromide form of the Amberlyst polymer or the chloride form (5.8 mmol). The mixture was stirred for 24 h, and then filtered. A Soxhlet extraction was used to recover as much product as possible. The product was isolated by distillation.

#### 2.12.9.1-Reduction of benzaldehyde

When using the bromide form of the Amberlyst polymer, the yield of dibenzyl ether was 65 % (1.21 g) when  $\text{Me}_2\text{HSiOTf}$  was used and 40 % (0.75 g) when  $\text{Me}_2\text{HSiCl}$  was used.

When using the chloride form of the Amberlyst polymer and  $\text{Me}_2\text{HSiCl}$ , the yield of dibenzyl ether was 45 % (0.84 g).

#### 2.12.9.2-Reduction of butanal.

When using the bromide form of the Amberlyst polymer, the yield of dibutyl ether was 51 % (0.9 g) when  $\text{Me}_2\text{HSiOTf}$  was used and 29 % (0.5 g) when  $\text{Me}_2\text{HSiCl}$  was used.

When using the chloride form of the Amberlyst polymer and  $\text{Me}_2\text{HSiCl}$ , the yield of dibutyl ether was 34 % (0.61 g).

#### 2.12.9.3-Reduction of hexanal

When using the bromide form of the Amberlyst polymer the yield of dihexyl ether was 58 % (1.05 g) when  $\text{Me}_2\text{HSiOTf}$  was used and 33 % (0.6 g) when  $\text{Me}_2\text{HSiCl}$  was used.

When using the chloride form of the Amberlyst polymer and  $\text{Me}_2\text{HSiCl}$ , the yield of dihexyl ether was 36 % (0.68 g).

#### 2.12.9.4-Reduction of octanal.

When using the bromide form of the Amberlyst polymer, the yield of dioctyl ether was 65 % (1.19 g) when  $\text{Me}_2\text{HSiOTf}$  was used and 36 % (0.66 g) when  $\text{Me}_2\text{HSiCl}$  was used.

When using the chloride form of the Amberlyst polymer and  $\text{Me}_2\text{HSiCl}$ , the yield of dioctyl ether was 39 % (0.74 g).

#### 2.12.9.5-Reduction of trimethylacetaldehyde.

When using the bromide form of the Amberlyst polymer the yield of di-bis-(2,2-dimethyl-propyl) ether was 42 % (0.77 g) when  $\text{Me}_2\text{HSiOTf}$  was used and 18 % (0.33 g) when  $\text{Me}_2\text{HSiCl}$  was used.

When using the chloride form of the Amberlyst polymer and  $\text{Me}_2\text{HSiCl}$ , the yield of di-bis-(2,2-dimethyl-propyl) ether was 25 % (0.46 g).

#### 2.12.9.6-Reduction of 2-methyl-butylaldehyde.

When using the bromide form of the Amberlyst polymer, the yield of di-bis-(2-methyl-butyl)-ether) was 60 % (1.1 g) when  $\text{Me}_2\text{HSiOTf}$  was used and 26 % (0.48 g) when  $\text{Me}_2\text{HSiCl}$  was used.

When using the chloride form of the Amberlyst polymer and  $\text{Me}_2\text{HSiCl}$ , the yield of di-bis-(2-methyl-butyl)-ether) was 31 % (0.57 g).

2.12.11-Reduction of ketones  $\text{R}_1\text{R}_2\text{C}=\text{O}$  with  $\text{Me}_2\text{HSiOTf}$  in chloroform under different conditions.

##### 2.12.11.1-Reduction of ketones with $\text{Me}_2\text{HSiOTf}$ in chloroform.

The ketone (5.1 mmol) in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature. 2 mole equivalent of  $\text{Me}_2\text{HSiOTf}$  (10.2 mmol) were added to the solution. Water (10 ml) was added and the mixture was extracted with diethyl ether (2×10 ml). The organic phase was dried with magnesium sulfate and the solvent removed under reduced pressure.

The mixture was analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

2.12.11.1.1-Reduction of cyclohexanone with  $\text{Me}_2\text{HSiOTf}$  in chloroform.

Bicyclohexyliden-2-one was obtained from this reaction and the NMR spectroscopy data were identical to the literature values<sup>63</sup>.

2.12.11.1.2-Reduction of acetophenone with  $\text{Me}_2\text{HSiOTf}$  in chloroform.

1,3-Diphenylbut-2-en-1-one was obtained from this reaction and the NMR spectroscopy data were identical to the literature values<sup>64</sup>.

2.12.11.1.3-Reduction of benzophenone with  $\text{Me}_2\text{HSiOTf}$  in chloroform.

Diphenylmethane was obtained from this reaction and the NMR spectroscopy data were identical to the literature values<sup>65</sup>.

2.12.11.2-Reduction of ketones with  $\text{Me}_2\text{HSiOTf}$  in chloroform in the presence of tetrabutylammonium triflate.

The ketone (5.1 mmol) in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature. 2 Mol equivalent of  $\text{Me}_2\text{HSiOTf}$  (10.2 mmol) were added to the solution, followed by the addition of 2 mol of tetrabutylammonium triflate (10.2 mmol). Water (10 ml) was added and the mixture was extracted with diethyl ether (2×10 ml). The organic phase was dried with magnesium sulfate and the solvent removed under reduced pressure.

2.12.11.2.1- Reduction of cyclohexanone with  $\text{Me}_2\text{HSiOTf}$  in chloroform and tetrabutylammonium triflate.

The reaction gave bicyclohexyliden-2-one as described in Section 2.12.11.1.1.

2.12.11.2.2- Reduction of acetophenone with  $\text{Me}_2\text{HSiOTf}$  in chloroform with tetrabutylammonium triflate.

The reaction gave 1,3-diphenyl-but-2-en-1-one as described in Section 2.12.11.1.2.

2.12.11.2.3- Reduction of benzophenone with  $\text{Me}_2\text{HSiOTf}$  in chloroform with tetrabutylammonium triflate.

Dibenzhydryl ether was obtained from this reaction and the NMR spectroscopy data were identical to the literature values<sup>66</sup>.

2.12.11.3-Reduction of ketones with  $\text{Me}_2\text{HSiOTf}$  in chloroform in the presence of tetrabutylammonium chloride or bromide.

The ketone (5.1 mmol) in a solution of chloroform (20 ml) was stirred under nitrogen at room temperature. 2 Mol equivalent of  $\text{Me}_2\text{HSiOTf}$  (10.2 mmol) were added to the solution, followed by the addition of 2 mol of tetrabutylammonium chloride (10.2 mmol) or bromide (10.2 mmol). Water (10 ml) was added and the mixture was extracted with diethyl ether (2×10 ml). The organic phase was dried with magnesium sulfate and the solvent removed under reduced pressure.



2.12.11.3.1- Reduction of cyclohexanone with  $\text{Me}_2\text{HSiOTf}$  in chloroform and tetrabutylammonium chloride or bromide.

The reaction gave bicyclohexyliden-2-one as described in Section 2.12.11.1.1

2.12.11.3.2- Reduction of acetophenone with  $\text{Me}_2\text{HSiOTf}$  in chloroform with tetrabutylammonium chloride or bromide.

The reaction gave 1,3-diphenyl-but-2-en-1-one as described in Section 2.12.11.1.2.

2.12.11.3.3- Reduction of benzophenone with  $\text{Me}_2\text{HSiOTf}$  in chloroform with tetrabutylammonium chloride or bromide.

The reaction gave dibenzhydryl ether as described in Section 2.12.11.2.3.

2.12.12-Reduction of epoxides: Styrene Oxide with  $\text{Me}_2\text{HSiOTf}$  or  $\text{Me}_2\text{HSiCl}$  in chloroform.

0.5 g of styrene oxide was mixed with two mol equivalent of  $\text{Me}_2\text{HSiOTf}$  (1.73 g) in chloroform (all the chemicals were handled in an inert atmosphere of dry nitrogen) and stirred overnight at room temperature. The mixture was washed with water (10 ml) and extracted with diethyl ether (2x10 ml). The analysis of the reaction mixture was carried out using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

All NMR spectroscopy data were identical to the literature values<sup>67</sup>.

# Chapter 3

## Chapter 3- Introduction to ionic liquids

This chapter will review the chemical and physical properties of ionic liquids, and the uses to which ionic liquids have been put as solvents for catalytic reactions.

### 3.1-The definition of ionic liquids.

Essentially, an ionic liquid is a liquid formed entirely of ions. However, they have very different physical properties compared to other ions in the liquid phase. Tissot based his definition on the conductivity of the liquids, stating that ionic liquids have a specific conductivity superior, or equal, to  $10^{-4} \text{ S cm}^{-1}$ . This definition included high melting salts such as potassium pyrosulfate and mixtures of inorganic salts such as copper, potassium and lanthanum chloride, also called “molten salts”.

### 3.2-The history of ionic liquids.

Ionic liquids are not new and some of them have been known for a long time; for example,  $[\text{EtNH}_3][\text{NO}_3]$  which as a melting point of  $12^\circ\text{C}$  was first described in 1914<sup>68</sup>.

The first research in this area involved the synthesis of ethylammonium nitrate

<sup>68</sup>. This salt is a liquid at room temperature and contains a small amount of

water<sup>69</sup>. The first ionic liquid with chloroaluminate ions was developed in 1948 by Hurlay and Wier at the Rice Institute in Texas and was used as a bath solution for electroplating aluminium<sup>70,71</sup>. However, this system did not receive a great deal of attention until the 1970's when the group of Osteryoung and Wilkes prepared the first room temperature liquid chloroaluminate melts<sup>72-74</sup>. In 1967, Swain *et al* described the use of tetra-*n*-hexylammonium benzoate as a solvent for kinetic and electrochemical investigation<sup>75</sup>. In the early 1980's the group of Seddon and Hussey began to use chloroaluminate melts as nonaqueous, polar solvents for the investigation of transition metal complexes<sup>76-79</sup>. The first publications in which ionic liquids were described as new reaction media and catalysts for organic synthesis appeared at the end of 1980's<sup>80,81</sup>. The use of ionic liquids as solvents for homogeneous transition metal catalysts was described for the first time in 1990, by Chauvin *et al* and by Wilke *et al*. Chauvin's group dissolved nickel catalysts in a weakly acidic chloroaluminate melt and investigated the activity of the resulting ionic catalyst solution towards the dimerization of propene<sup>82</sup>. Wilkes *et al* used the same media and studied ethylene polymerisation using Ziegler-Natta catalysts<sup>83</sup>. The concept of ionic liquids received a significant boost when in 1992 water stable ionic liquids were prepared<sup>84</sup>; the cations in these are most commonly the derivatives of organic ammonium salts such as 1-alkyl-3-methylimidazolium and N-alkylpyridinium. These cations are paired with anions such as halides, tetrafluoroborate, hexafluorophosphate, nitrate and trifluoromethanesulfonate. We shall start by describing the synthesis, properties and potential of these ionic liquids.

### 3.3-Chemical and physical properties.

Many modifications can be made to ionic liquids, to their size, shape, and to the nature of their cations and anions, such that they now constitute the largest group of non-aqueous solvent media available. The characteristics of the solvent can be specifically engineered by the careful combination of anion and cation. Different physical properties such as melting point, density, conductivity and viscosity can be achieved, as well as solubility, miscibility and reactivity which are all influenced by the type of ionic liquid used.

#### 3.3.1-The negligibly small vapour pressure of ionic liquids.

Ionic liquids are often composed of poorly co-ordinating ions, therefore they have a high conductivity and a small vapour pressure. Ionic liquids do not evaporate, so may be used on the bench or under high vacuum and thus have few containment problems<sup>85, 86</sup>.

#### 3.3.2-The conductivity of ionic liquids.

Ionic liquids possess, by definition, a conductivity superior or equal to  $10^{-4}$  S  $\text{cm}^{-1}$ , but parameters such as viscosity, liquid density, size and degree of dissociation also affect the conductivity. It is rather difficult to estimate the contribution of each parameter to the conductivity of a liquid. Proportionality between the conductivity of a liquid and the inverse of the viscosity has been observed for several liquids over a wide temperature range<sup>87,88</sup>. Similar examples of the conductivity of common ionic liquids and organic solvents are given in Table 42.

Ionic liquid	[C <sub>4</sub> mim][TfO]	[C <sub>4</sub> mim] [ N(Tf) <sub>2</sub> ]	[C <sub>4</sub> mim] [BF <sub>4</sub> ]	[C <sub>4</sub> Et][BF <sub>4</sub> ]
Conductivity/ mS cm <sup>-1</sup>	3.7	3.9	3.6	11.6
Reference	70	70	70	90

**Table 42: Conductivities of different ionic liquids and solvents.**

### 3.3.3-The polarity of ionic liquids.

Solvent polarity has a powerful influence on the outcome of chemical reactions.

As a result, the choice of a solvent for a particular application must be made with great care<sup>90</sup>. Carmichael and Seddon probed the polarity of ambient temperature ionic liquids based on the 1-alkyl-3-methylimidazolium cation using the solvatochromic dye Nile Red<sup>91</sup>.

A wide range of dialkylimidazolium cation derivatives with different anions was examined. For the [C<sub>4</sub>mim]<sup>+</sup> ionic liquids, the polarity decreases through the anion series nitrite, nitrate, tetrafluoroborate and hexafluorophosphate. This decrease in polarity correlates with increasing anion size, hence with the reduction in the effective anion charge density. Therefore [C<sub>4</sub>mim][NO<sub>3</sub>] is more polar than the [BF<sub>4</sub>] and [PF<sub>6</sub>] ionic pairs. A similar trend in the polarity of both tetrafluoroborate and hexafluorophosphate ionic liquids were observed on varying the 1-alkyl chain. In both cases, the polarity increases when changing from n = 4 to n = 6. For 1-alkyl-3-methylimidazolium ionic liquids, the polarity is predominantly determined by the anion for ionic liquids containing short 1-alkyl groups and by the cation for those containing long 1-alkyl groups. Wavelengths of maximum absorption ( $\lambda_{\text{max}}$ ) and molar transition energies ( $E_{\text{NR}}$ ) for Nile Red dissolved in ionic liquids are presented in the following table. Most ionic liquids are in the same polarity range as 2-

aminoethanol ( $E_{NR} = 214 \text{ kJ mol}^{-1}$ ) and the short chain alcohols ( $E_{NR} = 218 \text{ kJ mol}^{-1}$ ).

compounds	$\lambda_{max}$ (nm)	$E_{NR}$ (kJ mol <sup>-1</sup> )
[C <sub>4</sub> mim][BF <sub>4</sub> ]	550.8	217.2
[C <sub>6</sub> mim][BF <sub>4</sub> ]	551.9	216.8
[C <sub>8</sub> mim][BF <sub>4</sub> ]	549.5	217.7
[C <sub>4</sub> mim][PF <sub>6</sub> ]	547.5	218.15
[C <sub>6</sub> mim][PF <sub>6</sub> ]	551.7	216.8
[C <sub>8</sub> mim][PF <sub>6</sub> ]	549.8	217.6
[C <sub>4</sub> mim][NO <sub>3</sub> ]	555.7	215.3
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	548.7	218
2-aminoethanol	-	214.8
ethanol	-	218.2
1-butanol	-	218.5

**Table 43: Wavelengths of maximum absorption ( $\lambda_{max}$ ) and molar transition energies ( $E_{NR}$ ) for Nile Red dissolved in ionic liquids<sup>87</sup>.**

### 3.3.4-The melting point of ionic liquids.

The melting point is, at a known pressure, the temperature at which the solid and the liquid state of a compound are in equilibrium. Ionic liquids are salts with melting points below 100 °C. This occurs for a number of reasons, although the structure of both the cations and anions are key factors.

Ngo *et al* have examined the properties of a series of imidazolium ionic liquids and shown that the melting points decrease the larger and more asymmetrical the substituted cations. Ionic liquids containing the triflate anion were reported to melt closer to room temperature<sup>92, 93</sup>, as seen in entry 8 in Table 43.

Increasing the branching of the alkyl group results in higher melting points than the linear analogues<sup>92</sup>. Passing from n-propyl to an *iso*-propyl increases the melting point by 82 °C, as shown in Table 44 entries 2 and 3.

The lower melting points of ionic liquids containing NTf<sub>2</sub><sup>-</sup> or OTf<sup>-</sup> could be attributed to electron delocalization and the inability of the anion to form hydrogen bonds <sup>69</sup>.

Comparing the melting points of two similar cations, one with a fluorinated methyl group [C<sub>2</sub>mimPF<sub>6</sub>] and the other with a TfO<sup>-</sup> anion [C<sub>2</sub>mimOTf] reveals a 50 °C difference in the melting point between the two ionic liquids, as presented in Table 45 entries 1 and 7. It is thought that the fluorine atoms in [C<sub>2</sub>mimPF<sub>6</sub>] alter the electron density on the imidazolium ring and promote hydrogen bonding. Table 44 showed the different examples cited and others ionic liquids.

[C <sub>n</sub> mim][X] X =	PF <sub>6</sub>				BF <sub>4</sub>		NTf <sub>2</sub>	OTf	Cl
n =	2	3	iso-3	4	2	4	2	2	4
Melting point °C	58	40	102	10	11	-81	4	9	41
Reference	94	92	92	84	94	84	92	92	84

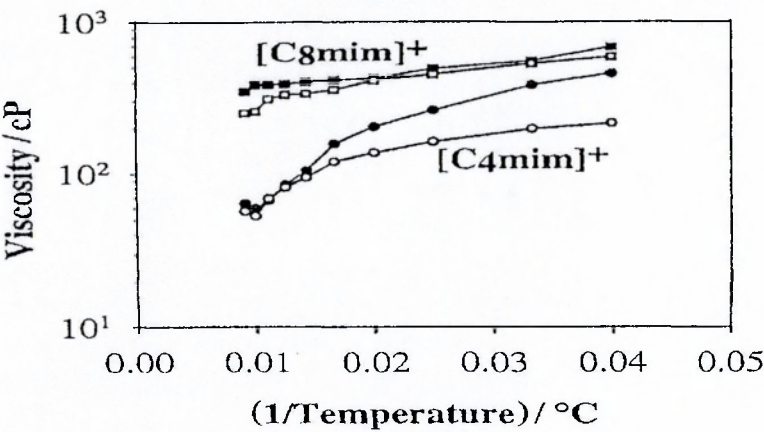
**Table 44: Melting point data for several ionic liquids.**

### 3.3.5- The viscosity of ionic liquids.

The viscosity of ionic liquids is several tens to several hundreds times greater than that of water at room temperature, as shown in Table 45. The structure of the cation strongly influences this viscosity. The lowest viscosity value obtained is for ethyl-methyl imidazolium salts, which combine sufficient side chain mobility with a low molecular weight. The viscosity increases with branching of the alkyl groups, due to the reduced rotational freedom. It has been pointed out that hydrogen bonding govern the viscosity of most ionic liquids<sup>94, 95</sup>.



Figure 10 shows that an increase in temperature leads to a decrease in the viscosity. Impurities in ionic liquids also have a significant effect on viscosity. Seddon *et al* reported the effect of water, as shown in Figure 10.



**Figure 10:** Viscosity of ionic liquids as a function of increasing the temperature: dried samples represented by filled symbols and water equilibrated sample by open symbols.

[C <sub>n</sub> mim][X] X = n =	PF <sub>6</sub>				BF <sub>4</sub>		NTf <sub>2</sub>		CF <sub>3</sub> CO
	4	4	6	8	2	4	2	4	2 4
Temperature □C	20	30	20	20	20	20	20	20	20
Viscosity /cP	371	204	680	866	66.5	154	44	52	90
Reference	96	96	96	96	96	96	68	94	94

**Table 45:** Viscosity data of several ionic liquids.

3.3.6- The density of ionic liquids.

The density of [C<sub>n</sub>mim]<sup>+</sup>-based ionic liquids is higher than that of water; thus, in a mixture they will form the lower phase. The molar mass of the anion significantly determines the overall density. Halogenated carborane anions have densities<sup>96</sup> that can be as high as 2.151g cm<sup>-1</sup>.

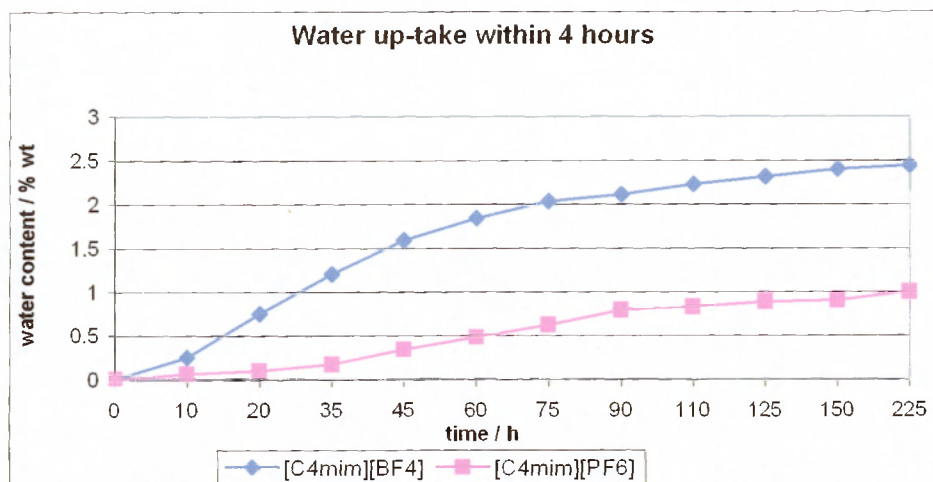
Adding CH<sub>2</sub> groups to the alkyl chains on the [C<sub>n</sub>mim]<sup>+</sup> cations decreases the density, as shown in the examples in Table 46. Shorter alkyl chain ionic liquids possess a higher density than the corresponding longer chain derivatives, which may be due to the ability of the shorter chains to close-pack. An increase in water content causes a decrease in the density such that it approaches that of water.

[C <sub>4</sub> mim][X] X =	Cl	BF <sub>4</sub>	OTf	PF <sub>6</sub>	NTf <sub>2</sub>	[C <sub>2</sub> mim][X] X =	BF <sub>4</sub>	PF <sub>6</sub>
Density/ g ml <sup>-1</sup>	1.08	1.12	1.29	1.36	1.43	Density/ <sub>1</sub> g mL <sup>-</sup>	1.17	1.37
Reference	84		69	84	69	Reference	97	

**Table 46: Densities at 25 °C of several ionic liquids.**

3.3.7- The water content of ionic liquids and solubility in other media

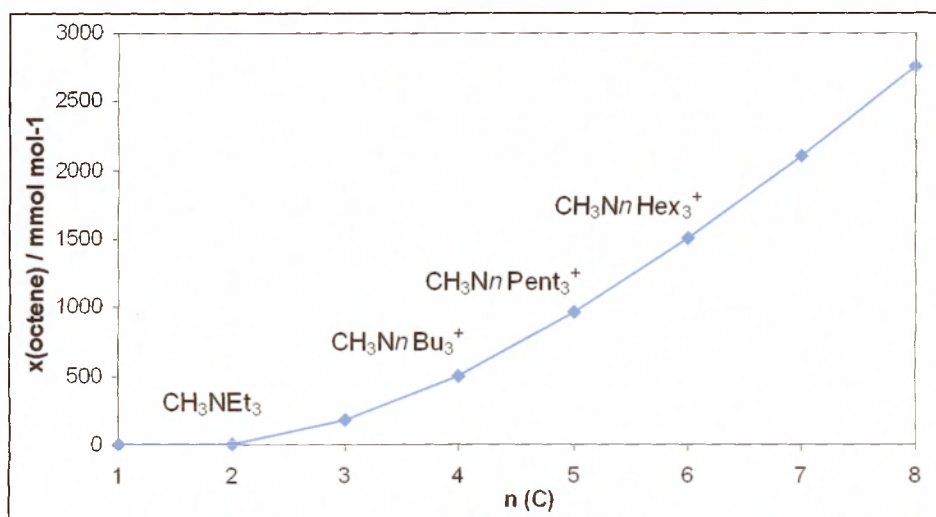
The identity of the anion greatly influences the water miscibility. It is important that the ionic liquid is dry since water interferes with the physical properties of the ionic liquids<sup>98</sup> The amount of water up-take from the atmosphere over four hours is shown in Graph 15 for two ionic liquids: [C<sub>4</sub>mim][BF<sub>4</sub>] which is soluble in water and [C<sub>4</sub>mim][PF<sub>6</sub>] which is not soluble in water.



Graph 15: Water content of two ionic liquids with time

Ionic liquids containing  $\text{BF}_4^-$  anions may be miscible with water, depending on the length of the alkyl chain; for example,  $[\text{C}_n\text{mim}][\text{BF}_4]$  ionic liquids with  $n > 6$  are not water soluble whereas those with  $n < 6$  are water soluble<sup>97</sup>

The solubility of ionic liquids in organic media was also studied; for example, the influence of the cation on the solubility of tosylate melts in 1-octene<sup>98</sup> is shown in Graph 16.



Graph 16: The solubility of 1-octene in different tri-*n*-alkyl-methyl-ammonium tosylate melts at 80 °C ( $n(\text{C})$  = number of carbons of the alkyl residue).

### 3.4-The synthesis and characterisation of ionic liquids.

#### 3.4.1-Preparation

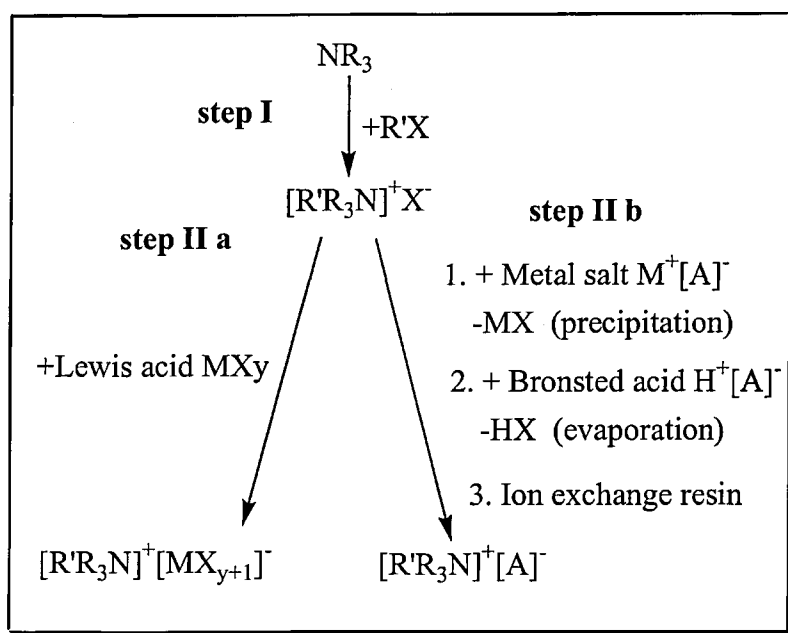
The initial step in the synthesis of ionic liquids is the quaternization of an amine, or phosphine, to form a cation<sup>74</sup> Salts with different anions are obtained from quaternization reactions by judicious choice of the alkylating agent. Examples of ionic liquids that can be prepared by direct quaternization are shown in Table 47.

Ionic liquids	[C <sub>4</sub> mim][Cl]	[Bu <sub>3</sub> NMe][OTs]	[Ph <sub>3</sub> POc][OTs]	[C <sub>2</sub> mim][OTf]
Alkylating agent	chlorobutane	MeOTs	OcOTs	methyl triflate
Melting point °C	65-69	62	70-71	-9
Reference	74	99	100	84

**Table 47: Examples of ionic liquids that can be formed by direct quaternization.**

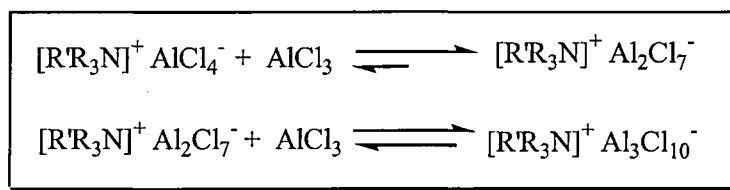
(Oc = octyl, Ts=H<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>, OTf = triflate)<sup>100</sup>

In some cases it is not possible to form the desired anion directly by quaternization, such that furthers steps are required. Starting from an ammonium halide [R'R<sub>3</sub>N]<sup>+</sup>X<sup>-</sup>, two different routes are possible, as shown in Scheme 24.



**Scheme 24: Synthetic routes for the formation of Ionic Liquids**

The ammonium halide can be treated with a Lewis acid  $\text{MX}_y$ , to give an ionic liquid of formula  $[\text{R}'\text{R}_3\text{N}]^+[\text{MX}_{y+1}]^-$ . Several anionic species are often present in an equilibrium which depends on the ratio of  $[\text{R}'\text{R}_3\text{N}]^+\text{X}^-$  and  $\text{MX}_y$  present. With an excess of the Lewis acid,  $\text{MX}_y$ , additional anionic species can be formed from further acid base reactions with the previously formed anion, as shown in Scheme 25<sup>101</sup>



**Scheme 25**

It is also possible to exchange the halide for another anion. This is achieved by the addition of a metal salt  $\text{M}^+\text{A}^-$ , which encourages the precipitation of  $\text{M}^+\text{X}^-$  during the reaction and the formation of  $[\text{R}'\text{R}_3\text{N}]^+\text{A}^-$ .

The synthesis of pure ionic liquids requires particular attention to the preparative procedure. Unfortunately, it is not possible, as with organic solvents, to purify the ionic liquids by distillation, so it is the selectivity of the synthesis that determines the purity of the ionic liquids.

#### 3.4.2-The handling and availability of ionic liquids.

The difficulty of handling ionic liquids depends essentially on the stability of the anion towards hydrolysis. Whereas ionic liquids based on nitrates, benzenesulfonates and bis[trifluoromethylsulfonyl]amide ions are air and water stable and can even be synthesised in water, systems involving the chloroaluminate anion are classified as extremely hygroscopic and labile towards hydrolysis.

In the presence of water, chloroaluminate melts react to release super-acidic protons. This causes unwanted side reactions and increases the potential for corrosion.

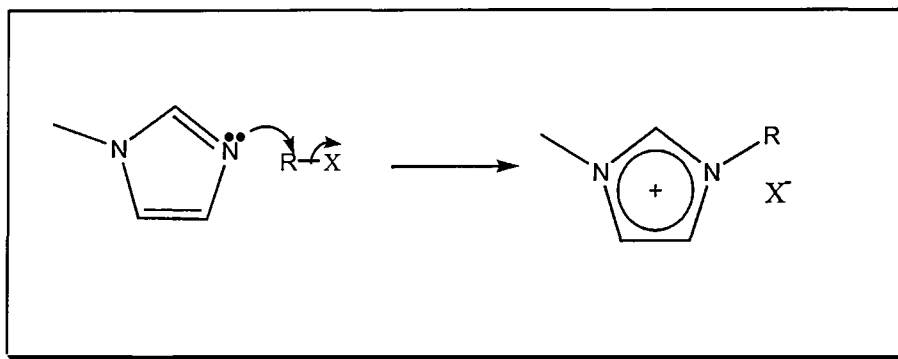
Organic nitrates and perchlorates are potentially explosive, especially when vigorously dried.

For the synthesis of  $C_4mimPF_6$ , some precautions need to be taken, such as using a plastic vessel and heating the mixture to not more than 50 °C, because of the formation of HF, which is highly corrosive, toxic and able to etch the glassware.

The commercial availability of ionic liquids was until recently very limited. Since 1999 a large variety of ionic liquids have become commercially available in up to litre quantities.

### 3.4.3-The reaction mechanism of ionic liquid formation.

The first step of the preparation of the ionic liquid usually involves the reaction of 1-methylimidazole with an alkyl halide. This reaction is known as the Menshutkin reaction and is a reversible reaction<sup>87</sup>. The mechanism is illustrated in Scheme 26.

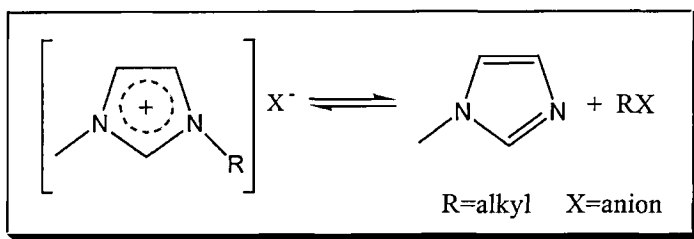


**Scheme 26: The mechanism of the Menshutkin reaction**

### 3.4.4- Impurities in ionic liquids.

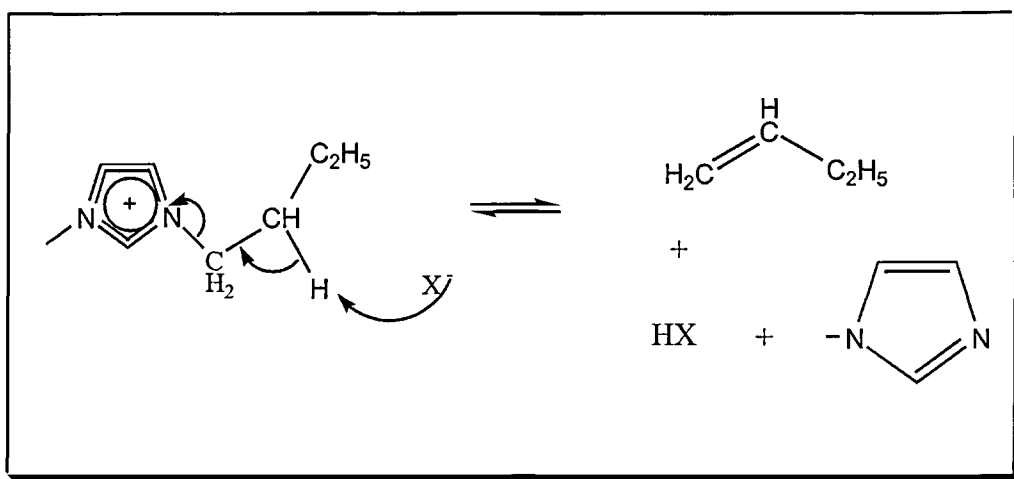
Ionic liquids may contain different amounts of impurities depending on the method of preparation. For example, in the drying stage, ionic liquids can change their colour. When a nitrate-base is heated above 80 °C at reduced pressure to remove water, the colour changes from colourless to brown. This is due to the formation of nitrogen oxide impurities from side reactions in the mixture.

Gale and Osteryoung<sup>102</sup> showed that impurities come from degradative side reactions. One of the most common of these side reaction is the reverse Menshutkin reaction<sup>103</sup>, where the halide attacks the alkyl group to give the starting material 1-methyl imidazole and the alkyl halide.



**Scheme 27: Reverse Menshutkin reaction.**

Another decomposition reaction is the Hofmann elimination, which forms 1-methylimidazole, together with an acid and an alkene.



**Scheme 28: Mechanism of the Hofmann elimination.**

The basicity of the anion has a direct effect on the Hofmann reaction. Alkene formation increases in the order  $[\text{NO}_3^-] < [\text{SCN}^-] < \text{I}^- < \text{Br}^-$  in the tetraalkylammonium salts.

The presence of impurities (water, halides, etc) in ionic liquids also changes the physico-chemical properties, as presented in different examples in Table 48<sup>97</sup>.

For example,  $[\text{C}_4\text{mimBF}_4]$  with a 0.01 molal chloride anion concentration has a viscosity of  $154 \text{ mPa s}^{-1}$  and an increase of the chloride anion concentration to



0.5 molal increases the viscosity to 201 mPa s<sup>-1</sup>, as shown in entry 2 in Table 48.

[C <sub>n</sub> mim][X] X =	BF <sub>4</sub>				NO <sub>3</sub>		
n =	2	2	4	4	4	4	8
Temperature °C	20	20	20	20	45	45	20
[Cl <sup>-</sup> ]/ mol kg <sup>-1</sup>	0.01	1.8	0.01	0.5	0.02	1.7	0.01
Viscosity / mPa s <sup>-1</sup>	66.5	92.4	154	201	67	223	1238

**Table 48: Comparison of the viscosity of high chloride ion and low chloride ion contaminated ionic liquids<sup>96</sup>.**

Each batch of ionic liquids has to be characterised for water content and the concentration of halides, to ensure the reproducibility of reactions. The water content is determined by a Karl Fisher titration and the halide content is analysed by the wet chemical method of Vollhard, or using a chloride ion selective electrode for chloride content.

### 3.5-Ionic liquids as solvents for catalytic reactions.

Ionic liquids are able to dissolve organometallic compounds and are therefore good solvents for reactions involving homogeneous catalysts. Ionic liquids can behave as an inert solvent or as a co-catalyst. When it acts as a solvent, the role of the ionic liquid is to provide a polar, weakly co-ordinating medium for the transition metal catalyst, reagents or products. The ionic liquids provide different chemical and physical environment for a reaction, which will be not possible with water or common organic solvents. Ionic liquids formed by the reaction of a halide with a Lewis acid can also act as co-catalyst.

The obvious advantage of ionic liquids, besides not being volatile, is that they permit biphasic reactions with an ionic catalyst phase. The result is a catalyst that can be easily recycled.

In the following section an overview of recent work on the use of transition metal catalysts in ionic liquids is presented.

### 3.5.1 Hydrogenation reactions.

Many attempts have been made to develop biphasic processes for homogeneous hydrogenation catalysed by transition metal complexes. In 1995 Chauvin<sup>104</sup> carried out the first successful hydrogenation reaction in ionic liquids. Chauvin and co-workers dissolved the cationic “Osborn complex”  $[\text{Rh}(\text{nbd})(\text{PPh}_3)_2]\text{PF}_6$  (nbd = norbadiene) in ionic liquids based on weakly co-ordinating anions, and used it as the catalyst precursor for the hydrogenation of pent-1-ene using dihydrogen. This reaction using  $[\text{bmim}]\text{SbF}_6$  is five times faster than that using acetone as solvent. Similarly, De Souza *et al* investigated the reactivity of the Wilkinson-catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$  in the hydrogenation of cyclohexene in  $[\text{C}_4\text{mim}][\text{BF}_4]$ <sup>105</sup>.

The hydrogenation of butadiene and 1-hexene with rhodium and cobalt has also been reported<sup>106, 107</sup>. Similarly the ruthenium catalysed hydrogenation of aromatic compounds<sup>108</sup> and acrylonitrile-butadiene co-polymers<sup>109</sup> have been successful in ionic liquids.

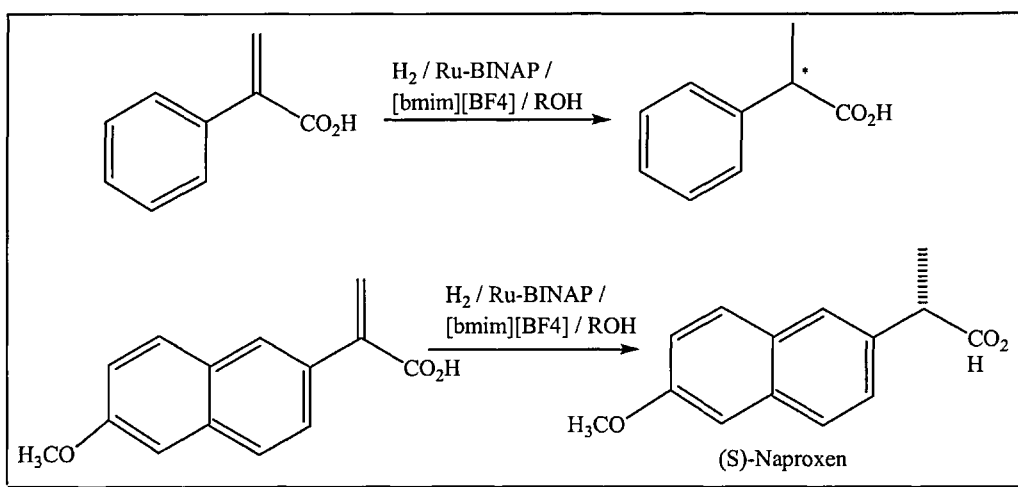
Hydrogenation of buta-1,3-diene to but-1-ene with dihydrogen was studied using either  $\text{RuCl}_2(\text{PPh}_3)_3$  or  $\text{K}_3[\text{Co}(\text{CN})_5]$ <sup>110</sup>. Depending on the catalyst used,

the hydrogenation gave different products: the ruthenium-based catalyst unselectively yielded a mixture of but-1-ene, *cis* and *trans* but-2-enes and butane, whereas the cobalt-based catalyst gave selectively but-1-ene at 25 °C. Palladium (II)(acac)<sub>2</sub> catalysed the hydrogenation of buta-1,3-diene to butenes at 50 °C under several bar of dihydrogen <sup>111</sup>. For comparison purposes, the same reaction was carried out in dichloromethane, and similar selectivities for butenes was achieved by Pd(acac)<sub>2</sub> when using ionic liquids and the organic solvent. No significant change in selectivity was observed by changing the temperature, hydrogen pressure or catalyst concentration, but the latter did affect the reaction time which dropped from 65 min (for [diene]/[Pd] = 1450), to 6 min (for [diene]/[Pd] = 138). In conclusion, the mechanism of the hydrogenation reaction for the palladium complex dissolved in ionic liquids was thought to be analogous to the one-phase reaction. The catalytic system promoted the selective reduction of functionalized dienes to monoenes without the competitive reduction of acid, ester or nitro groups.

Arene hydrogenation in a room temperature ionic liquid using a ruthenium catalyst was also studied. The [H<sub>4</sub>Ru<sub>4</sub>(η<sup>6</sup>-arene)][BF<sub>4</sub>]<sub>2</sub> cluster, which is soluble and stable in [bmim][BF<sub>4</sub>], was used as the catalyst precursor for the hydrogenation of benzene, toluene and cumene (*iso*-propylbenzene). The reaction occurred with 60 atm of dihydrogen, at 90 °C, in about 2h 30 min, to give 91 %, 72 % and 34 % conversion respectively for benzene, toluene and cumene. Hydrogenation of these arenes was carried out with the same catalyst precursor but in aqueous media and gave a similar percentage of conversion. The advantage of ionic liquids is that it is easy to remove traces of organic

compounds. You can thus repeatedly use the same batch of ionic liquid for the catalytic hydrogenation of several different arenes.

The ruthenium complex  $[\text{RuCl}_2\text{-(S)-BINAP}]_2\text{NEt}_3$  is another type of catalyst precursor which can be dissolved in  $[\text{bmim}][\text{BF}_4]$  and an alcohol; it is able to catalyse the hydrogenation of 2-arylacrylic acids (where aryl is equal to phenyl or 6-methoxynaphthyl), as shown in Scheme 29. An alcohol solvent was used to obtain a two phase reaction, where the hydrogenated product was in the organic phase and the catalyst stays in the ionic liquid phase. Use of methanol gave (S)-2-phenylpropionic acid with an 83 % ee and *isopropanol* afforded a 64 % ee. This catalytic system was also applied to the hydrogenation of 2-(6-methoxy-2-naphthyl) acrylic acid to give (S)-Naproxen in 80 % ee.



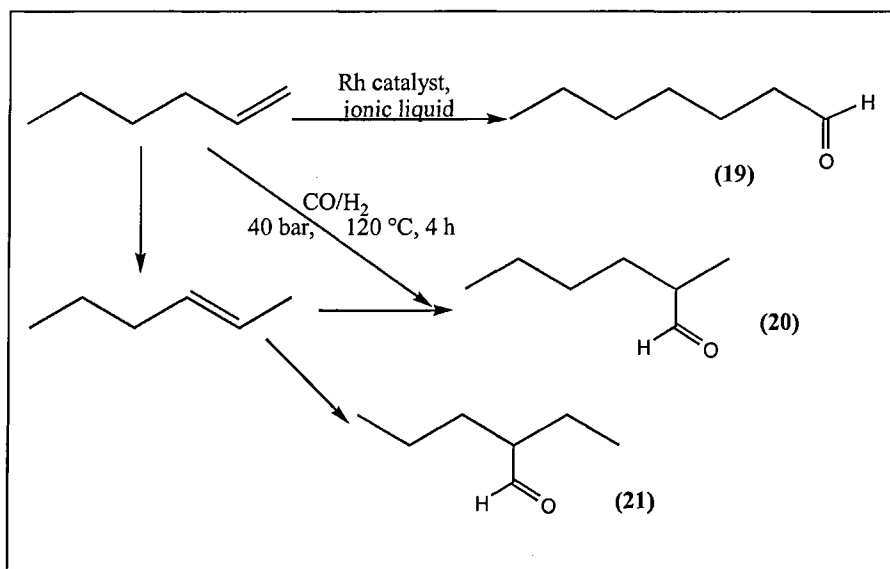
**Scheme 29: Hydrogenation of 2-arylacrylic acids.**

### 3.5.2 Hydroformylation reactions.

Following the hydrogenation reaction, Chauvin also examined the hydroformylation of pent-1-ene using a  $[\text{Rh}(\text{CO})_2(\text{acac})/\text{PPh}_3]$  catalyst precursor. The product hexanal is not soluble in ionic liquids, which enables its

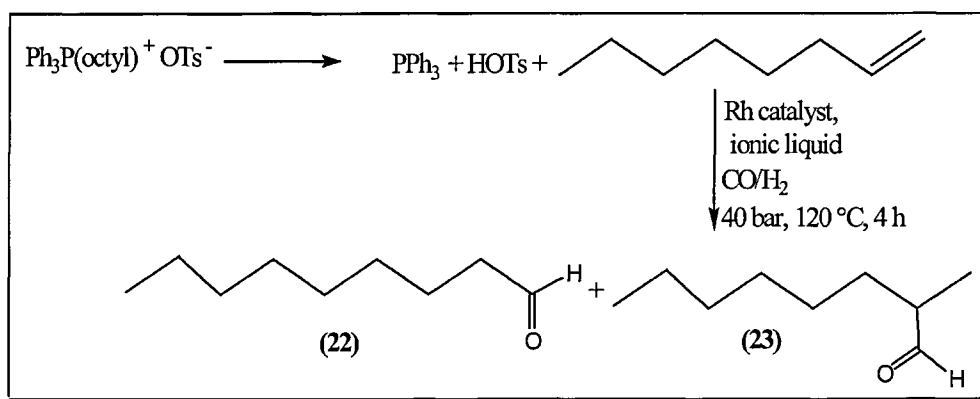
simple isolation. The reaction gave the highest yield of hexanal (99%) using a [bmim][PF<sub>6</sub>] ionic liquid. A small part of the active rhodium is extracted when removing the organic product. Thus, the catalyst precursor has to be immobilised in the ionic liquid using a more polar ligand on the metal. Monosulfonated or trisulfonated triphenylphosphine ligands were used since their solubility in the ionic liquid is higher than in hexanal. The use of these types of catalyst precursor results in the decrease of the catalytic activity of the rhodium and so a lower catalytic reaction rate. Both catalysts gave a 3:1 ratio of the respective products hexanal: 2-methylpentanal.

High-melting phosphonium tosylates can also be used as the solvent in catalytic hydroformylation reactions. Tetraalkylphosphonium tosylate was synthesised and used for the hydroformylation of hex-1-ene in the presence of rhodium catalysts with or without phosphine ligands. The reaction is shown in Scheme 30:



**Scheme 30: Hydroformylation of hex-1-ene.**

Hex-1-ene gave heptanal (**19**) and the branched product 2-methylhexanal (**20**). The products (**20**) and (**21**) were produced by the hydroformylation of hex-2-ene, derived from the isomerisation of hex-1-ene. Using  $[\text{Rh}_2(\text{OCH}_3\text{CO}_2)_4]$  as the catalyst gave 80 to 96 % conversion, depending on the alkyl group of the phosphonium salt. When the alkyl group on the phosphorus is too bulky, for example octyl, the reaction undergoes an elimination to form the corresponding alkene, which is then hydroformylated to the corresponding aldehyde as shown in Scheme 31:



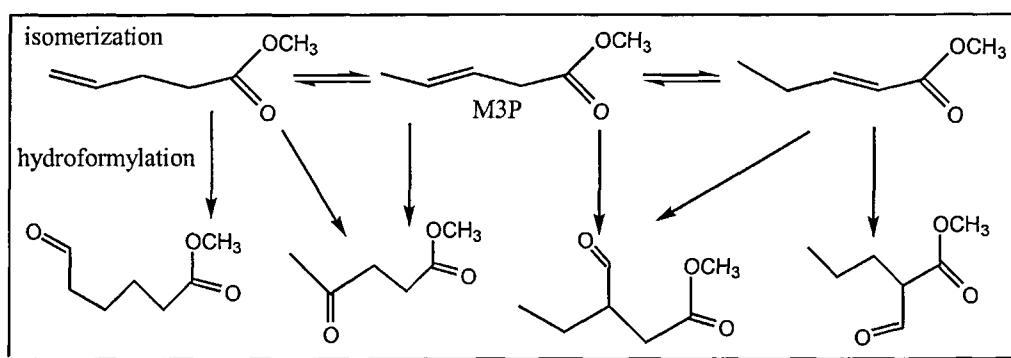
**Scheme 31: Hydroformylation of octene.**

The product distribution is dependant on the ionic liquid used. The ratio (**19**): (**20+21**) is equal to 1:4 when  $\text{Ph}_3\text{P}(\text{butyl})^+ \text{OTs}^-$  was used, whereas  $\text{Bu}_3\text{P}(\text{ethyl})^+ \text{OTs}^-$  led to the formation of the linear isomer as the major product, with a ratio of 2.5:1. So the reaction regioselectivity can be controlled by the choice of solvent.

The addition of a phosphine ligand to the rhodium catalyst, e.g.  $(\text{Ph}_3\text{P})_3\text{Rh}(\text{CO})(\text{H})$ , led to an increase in the product yield for all types of ionic liquid used and a preference for the linear isomer, the ratio changing from 1:4 to 1:3.2.

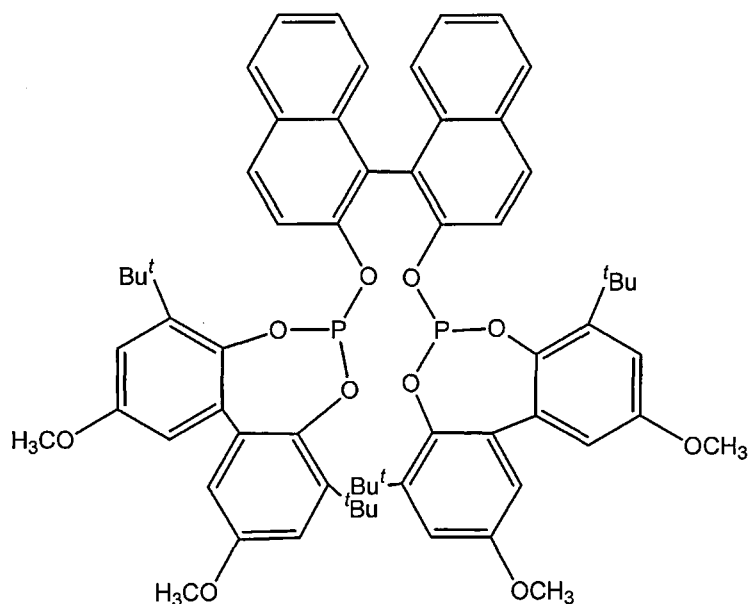
The organic products were analysed for rhodium content, and showed negligible amounts of the metal, indicating that the rhodium stayed in the ionic liquid phase.

Keim *et al* chose rhodium for the hydroformylation of methyl-3-pentenoate (M3P) in the presence of CO/H<sub>2</sub><sup>112</sup>. The hydroformylation of M3P is particularly interesting because it is an industrially important olefin and does not form a biphasic reaction mixture with ionic liquids. Scheme 32 shows the different products obtained in this hydroformylation:



**Scheme 32: Hydroformylation of methyl-3-pentenoate**

The ratio of products obtained depends upon the ligand on the rhodium catalyst. If the rhodium has a phosphine ligand the ratio *n*:*i* ( *n*-hydroformylated product to *iso*- hydroformylated product) is 1:10. This ratio changes to 1:1 in the case of the 2,2'-bis{((2,2'-bis(4-methoxy-6-*t*butyl) phenoxy) phosphino)-oxyl}-1,1'-binaphthyl ligand, shown in Figure 11.



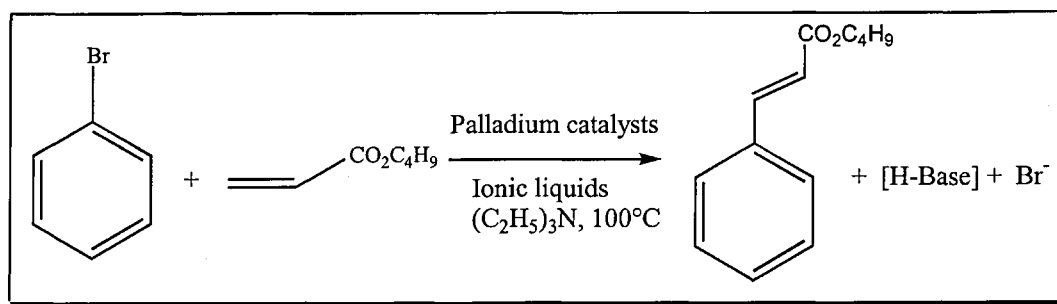
**Figure 11**

To examine the influence of the solvent, the reaction was carried out in [bmim][PF<sub>6</sub>] and toluene solvents. The regioselectivity did not change, but the turnover frequency doubled when using the ionic liquid. The remaining ionic catalyst phase is still active after the product separation and can be reused for catalysis. Unfortunately, the catalytic activity decreases considerably, to almost no activity after four cycles.

### 3.5.3-The Heck reaction.

Kaufmann *et al* investigated the use of molten salts to carry out the Heck reaction<sup>113</sup>. The Heck reaction proceeded in the melt hexadecyltributylphosphonium bromide, tetrabutylammonium bromide and tetraoctylammonium bromide with a high yield. Bromobenzene reacted with *n*-butyl acrylate in phosphonium salts at 100 °C, in the presence of palladium catalysts and triethylamine, yielding the *n*-butyl *trans*-cinnamate.





**Scheme 33: Formation of n-butyl *trans*-cinnamate via the Heck reaction in ionic liquid**

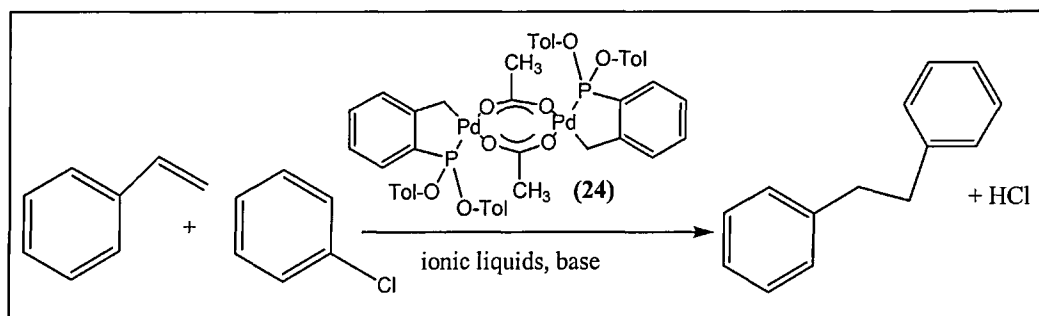
Several palladium catalysts were used such as  $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$  and  $\text{Pd}(\text{OCO}_2\text{CH}_3)_2$  which formed a homogeneous stable solution in the molten salts.  $\text{PdCl}_2$  is also a palladium(0) catalyst precursor for the Heck reaction, but after a few hours it precipitated as a palladium cluster. This precipitation did not occur with the other two palladium catalysts, highlighting the stabilising effect of the ammonium or phosphonium salt on the catalyst.

In the case of the phosphonium salt, after distillation of the products, the remaining catalyst can be used for two more runs without decreasing the catalytic activity in the melt. The yield obtained is 80-99 % over 6 to 24 h.

The Heck coupling of aryl halides or benzoic anhydrides with alkenes can be performed, in the presence of a  $\text{PdCl}_2$  or  $\text{Pd}(\text{OAc})_2$  catalyst and a base, in excellent yields at room temperature in ionic liquids<sup>113</sup>. The efficiency of the Heck reaction was examined in different types of ionic liquids, for example, using cation  $[\text{bmim}]$  = 1-butyl-3-methylimidazolium, 1-pentyl-3-methylimidazolium or N-hexylpyridinium  $[\text{C}_6\text{py}]$  as the cation, and chloride, hexafluorophosphate or tetrafluoroborate as the anion. The reaction of iodobenzene with ethyl acrylate formed *trans*-ethyl cinnamate in 99 % yield at

40 °C when the reaction was carried out in chloride salts and the [C<sub>6</sub>py] cation gave a higher yield than [bmim]. Addition of a phosphine ligand to the palladium decreases the yield of the reaction, and higher temperature (100 °C) ensures the reaction goes to completion. When the reaction was carried out with [PF<sub>6</sub>]<sup>-</sup> and [BF<sub>4</sub>]<sup>-</sup> anions, a higher temperature was needed (80 °C) and the addition of a phosphine ligand increased the reaction rate.

Böhm and Herrmann tried an alternative catalyst for the Heck reaction, the cyclometallated complex (**24**) with aryl bromides and aryl chloride in different ionic liquids, as shown in Scheme 34.



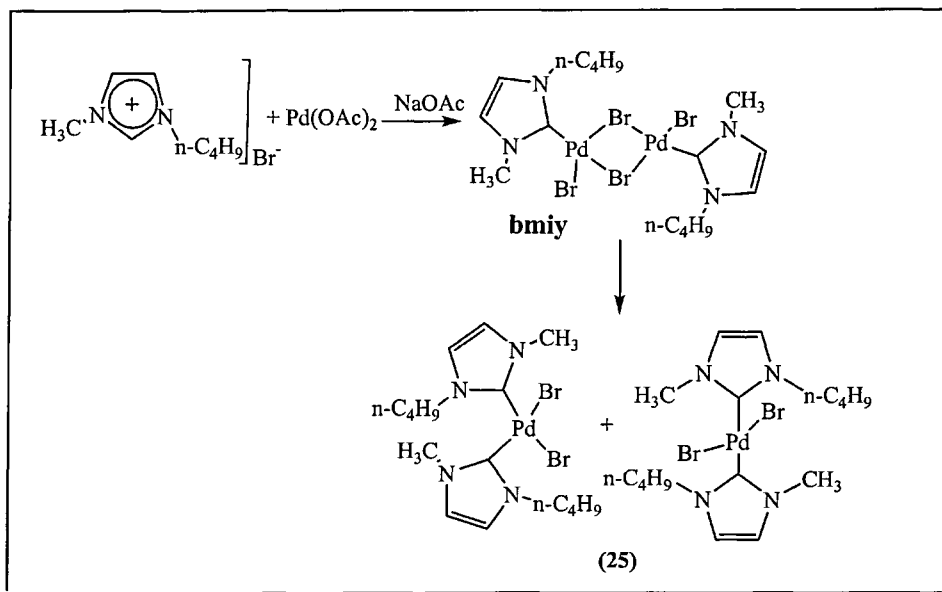
**Scheme 34: An example of the Heck reaction using a different metal complex catalyst.**

They found that an alkylammonium ionic liquid gave a higher percentage yield and conversion than the imidazolium ionic liquids, from 22 % for the latter up to 52 % for the former.

Xu *et al* compared the two ionic liquids [bmim][Br] and [bmim][BF<sub>4</sub>] in the Heck reaction. They found that the Heck reaction proceeded more readily in [bmim][Br] than in [bmim][BF<sub>4</sub>]. A 100 % conversion of the halide was achieved with 99 % selectivity for the formation of *trans*-stilbene when the

reaction was carried out in [bmim][Br], whereas 21 % conversion with 92 % selectivity was obtained with [bmim][BF<sub>4</sub>] using the same conditions. They also found that [bmim][Br] reacts with the catalyst Pd(OAc)<sub>2</sub> to give an N-heterocyclic carbene complex of palladium, but this reaction did not occur in [bmim][BF<sub>4</sub>]. In the case of [bmim][BF<sub>4</sub>], palladium black slowly precipitated, indicating the decomposition of the active palladium species<sup>113, 114</sup>. Furthermore, this palladium complex has been shown to be an active catalyst for the Heck reaction<sup>114-116</sup>.

When Pd(OAc)<sub>2</sub> was heated in [bmim][Br] in the absence of an olefin or aryl halide, under conditions otherwise similar to those used in the Heck reaction, a colour change was observed in a few minutes from dark brown to red and then to yellow. The yellow solution suggested the formation of the N-heterocyclic 1-butyl-3-methylimidazol-2-ylidene complex (**bmiy**), which is catalytically active for C=C double bond forming reaction. A transformation of **bmiy** into the two isomers (**25**) was subsequently observed. Longer reaction time showed the disappearance of **bmiy**, Scheme 35, which suggests that these isomers (**25**) are immediate catalyst precursors for the Heck reactions. It was not surprising that complexes (**25**) catalysed the olefination reactions of aryl halides.



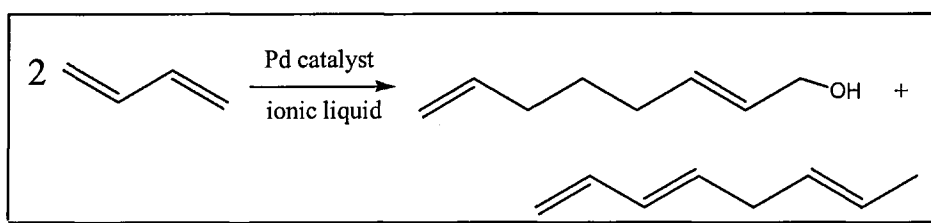
**Scheme 35**

It is often difficult to compare and contrast many of the publications in this area since the authors use different catalysts, different types of ionic liquid and different conditions. However, it is clear from these studies that the nature of the anion and cation in the ionic liquid can exert a marked effect on the rate of the reaction, and how the catalyst precursor dissolves in the ionic liquid phase. In all cases it has been shown that ionic liquids are attractive alternatives to volatile organic solvent for catalytic reactions as they permit a multiple phase reaction where the catalyst remained in the ionic liquid phase, is able to be reused and is still active for a few cycles. Separation of products is easier and can lead to a higher yield in the reaction.

#### 3.5.4-The hydrodimerisation reaction.

The homogeneous catalytic hydrodimerisation of 1,3-butadiene with soluble palladium complexes in the presence of carbon dioxide affords, in most cases, octa-2,7-dien-1-ol<sup>1118,1119</sup>. Dullius *et al* reported the use of [bmim][PF<sub>6</sub>] and

[bmim][BF<sub>4</sub>] for the hydrodimerisation of 1,3-butadiene without carbon dioxide, in the presence of palladium catalysts, as shown in Scheme 36. Palladium complexes such as  $[(\eta^3\text{-C}_4\text{H}_7)\text{Pd-}\mu\text{-Cl}]_2$ ,  $[(\eta^3\text{-C}_4\text{H}_7)\text{Pd}(1,5\text{-cyclooctadiene})][\text{BF}_4]$  and palladium acetate are soluble and stable in ionic liquids and can be used as catalyst precursors for the hydrodimerisation reaction. Octa-2,7-dien-1-ol and 1,3,6-octatriene are the major products obtained, with 40 % conversion and in a ratio of 9:1.

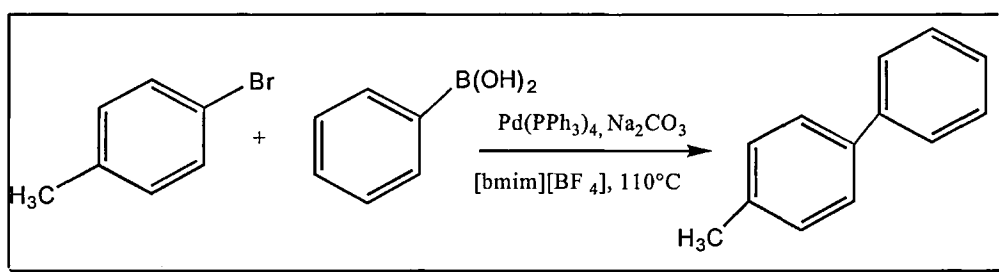


**Scheme 36: Hydrodimerisation of 1,3-butadiene**

Both of the products are soluble at room temperature but insoluble below 5 °C, so easy separation can be achieved by a simple decanting of the mixture at temperatures below 5 °C. Increasing the temperature from 40 °C to 70 °C leads to a small increase in the yield but no change in the selectivity. At 100 °C there is a dramatic decrease in the 1,3-butadiene conversion, from 40 % to 19 %. Atomic absorption analysis of the palladium content in the ionic liquid and in the organic phase shows that 97 % of the palladium is retained in the ionic phase. The recovered ionic catalyst can be reused several times (at least four) without loss of catalytic efficiency.

### 3.5.5-The Suzuki cross-coupling reaction.

The Suzuki cross-coupling reaction is an extremely versatile methodology for the generation of new carbon-carbon bonds and is employed in the synthesis of biaryls<sup>121</sup>. The reaction suffers from a number of drawbacks such as catalyst leaching into the organic layer, catalyst decomposition and poor solubility of reagents. To alleviate these problems, the reaction of 4-bromotoluene with phenylboronic acid was carried out in [bmim][BF<sub>4</sub>] using the original Suzuki conditions, as shown in Scheme 39<sup>121</sup>. This afforded the 4-methylbiphenyl in 30 % yield after 6 h, together with the observation of catalyst decomposition by precipitation of a black solid. This decomposition could be avoided by forming a catalyst precursor by heating the catalyst at 110 °C with the arylhalide in [bmim][BF<sub>4</sub>]. Once the catalytic solution had been generated the reaction could be carried out under air, and was started by the addition of arylboronic acid and Na<sub>2</sub>CO<sub>3</sub><sup>122</sup>.



Scheme 37

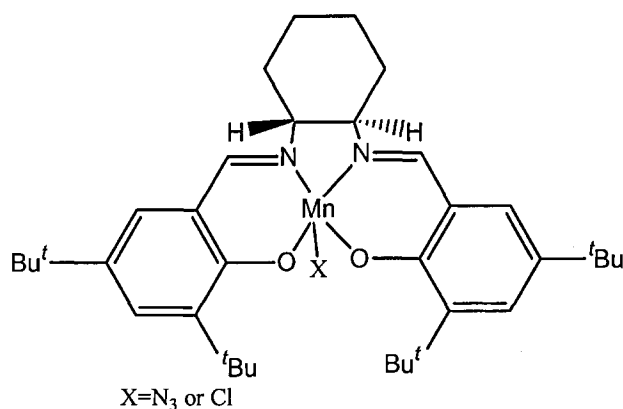
Adopting this procedure, the reaction gave the same product in 69 % yield after 10 min and without any catalyst decomposition. Reducing the catalyst concentration also increased the yield of the reaction.

Others aryl halides were used for the reaction, for example, bromobenzene was used with phenylboronic acid under the original Suzuki conditions ([Pd(PPh<sub>3</sub>)<sub>4</sub>]

= 3 mol %) which gave the biphenyl in 88 % yield in 6 h, whereas with [bmim][BF<sub>4</sub>] ([Pd(PPh<sub>3</sub>)<sub>4</sub>] = 1.2 mol%), a 93 % yield was obtained in 10 min. In conclusion, a higher yield and a significant increase in reactivity were obtained by using low concentrations of catalyst and ionic liquid solvents. The catalytic solution can be reused without loss of activity.

### 3.5.6-Oxidation reactions.

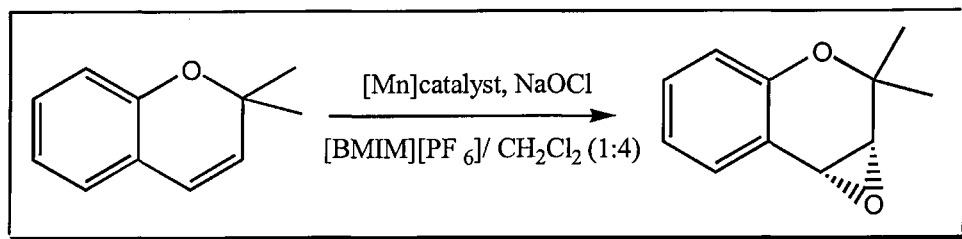
[bmim][PF<sub>6</sub>] was used to immobilise the Jacobsen's chiral (salen)Mn<sup>III</sup> epoxidation catalyst shown in Figure 12, which can be used for asymmetric epoxidations.



**Figure 12**

Reactions with 2,2-dimethylchromene, 6-cyano-2,2-dimethylchromene and indene as substrates, in the presence of 4 mol % of manganese catalyst and NaOCl as the oxidant, were carried out in [bmim][PF<sub>6</sub>]/CH<sub>2</sub>Cl<sub>2</sub> at 0 °C <sup>123</sup>.

Conversion of alkenes into epoxides was observed in 80 % yield with a good enantioselectivity (90 % ee), as presented in Scheme 38.



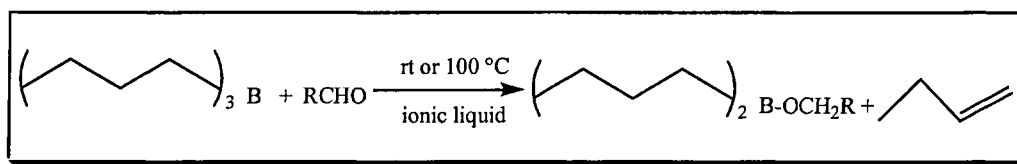
**Scheme 38: Conversion of alkenes into epoxides**

The reaction in the presence of ionic liquids is faster than without the ionic liquid. For example, epoxidation of 2,2-dimethylchromene required 6 h without ionic liquid and only 2 h with ionic liquid. The catalyst is recovered after extraction and reused for further catalytic reactions. Repeating the reaction five times resulted in a decrease in activity lowering the yield from 86 % to 53 %. This is possibly due to the degradation of the catalyst.

### 3.5.7-Reduction reactions.

Reduction of aldehydes by boron hydrides is an important organic transformation that requires a high temperature (approximately 150 °C).

Kabalka *et al* found that [bmim][BF<sub>4</sub>], [emim][BF<sub>4</sub>] and [emim][PF<sub>6</sub>] improved the rate of trialkylborane reductions of aldehydes<sup>124</sup>.



**Scheme 39**

For example, the reduction of benzaldehyde in [emim][PF<sub>6</sub>] occurred at room temperature giving 40 % yield after 24 h; this can be boosted to 100 % yield by



running the reaction at 100 °C for 16 h. As before, separation of the products is easy.

### **3.6-Conclusions.**

In the examples of transition metal catalysis described above, there is a marked improvement when the reaction is carried out in ionic liquids, leading to an increase in the yield or higher selectivity. The most important feature is the immobilisation, by dissolution, of the catalyst in the ionic liquid phase, after distillation of the products, leaving the catalyst behind for recycling. Thus, the catalyst can be reused several times in these catalytic reactions. As reported in the Heck reaction, the nature of the cation and anion can affect on the formation of the catalytically active species.

While we have seen that the physical properties of ionic liquids are highly influenced by the presence of impurities, the effect of impurities on the outcome of such catalytic reaction has not been mentioned in the literature.

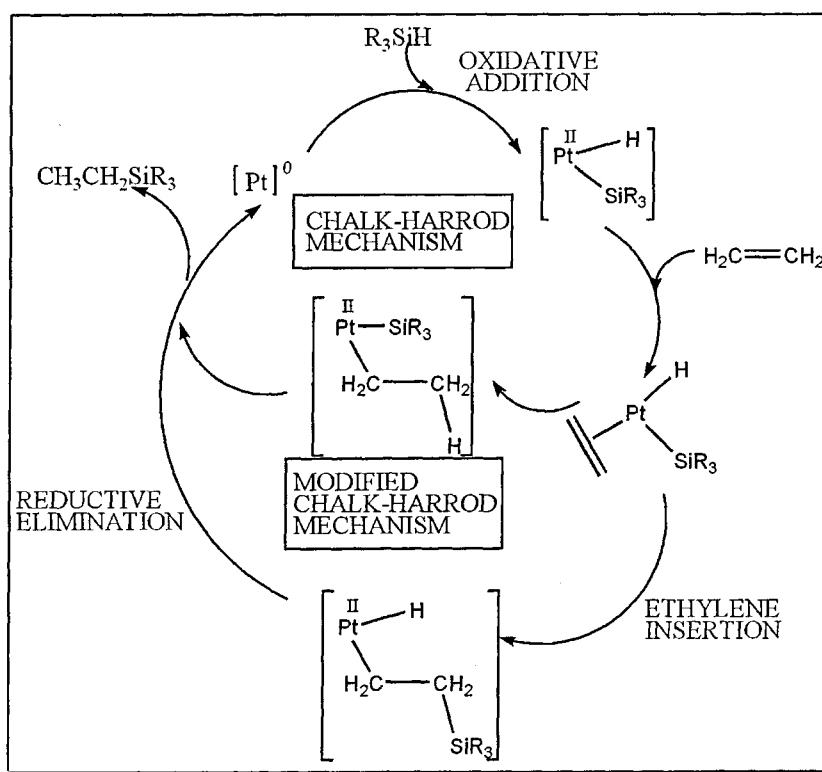
### **3.7- Transition metal catalysed hydrosilylation.**

The hydrosilylation of alkenes, carbonyl groups and related compounds is of considerable importance since organosilicon derivatives constitute useful intermediates in synthetic organic chemistry. For this reason, hydrosilylation reactions have been widely investigated and a considerable amount of work has been devoted to the elucidation of their reaction mechanisms.

Sommer and co-workers were the first to discovered the hydrosilylation reaction in 1947, when they reacted trichlorosilane with 1-octene<sup>125</sup>. This reaction

proceeds *via* a free radical reaction, and, based on this mechanism, a number of refinements and developments were achieved.

Speier's catalyst<sup>126-128</sup> is one of the most important non-radical catalysts for the platinum catalysed hydrosilylation of alkenes. This homogeneous catalyst is known as hexachloroplatinic acid, which contains a  $\text{Pt}^{\text{IV}}$  centre that can be readily reduced to provide the catalytically active  $\text{Pt}^{\text{II}}$  species<sup>124</sup>. A possible mechanism for the hydrosilylation of alkenes has been proposed by Chalk and Harrod that involves the oxidative addition of Si-H to the metal and alkene insertion into the metal-hydride bond, followed by a Si-C reductive elimination<sup>1</sup>. A modified Chalk-Harrod mechanism was subsequently proposed to explain the formation of vinylsilane, which involves ethylene insertion into a metal-silicon bond followed by a C-H reductive elimination (Scheme 40). In both cases, there is an initial induction owing the reduction of a  $\text{Pt}^{\text{IV}}$  complex to the  $\text{Pt}^{\text{II}}$  species by isopropanol.



**Scheme 40: The Chalk-Harrod and modified Chalk-Harrod mechanism.**

Although several experimental studies addressing the mechanism of hydrosilylation have been performed, including the use of ruthenium, rhodium, iridium, palladium and zirconium based catalysts, it is still not clear which of the two possible mechanisms is the most favourable. One suggestion is that, depending on the particular catalyst, a specific pathway is preferred. Several issues are not addressed by this mechanism; for example, the reaction mixture often becomes discoloured and a change from colourless to yellow, and in some extreme cases a black solution, has been observed. A requirement of oxygen was also noticed. The steric and electronic effect of the functional groups can also determine the mode of addition observed, which is not considered in the Chalk-Harrod mechanism.

A detailed theoretical investigation was performed on all the transition states and intermediates involved in: 1) the Si-H oxidative addition of H-SiR<sub>3</sub> (R = H,

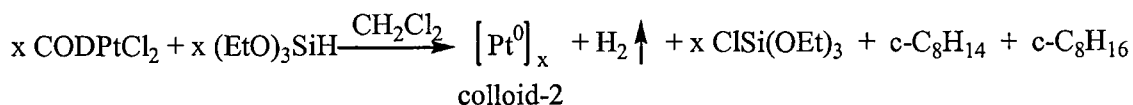
Cl, Me) to Pt (PH<sub>3</sub>)<sub>2</sub>; 2) the ethylene insertion into Pt-H and Pt-SiR<sub>3</sub> bonds; 3) the isomerization of the ethylene insertion product and 4) the Si-C and C-H reductive elimination <sup>129</sup>.

- 1) In the Chalk-Harrod mechanism, the rate-determining step is the isomerization of the Pt(SiR<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>)(PH<sub>3</sub>) complex, formed by the ethylene insertion into a Pt-H bond and its activation barrier is 22 kcal/mol for R = H, 23 kcal/mol for R = methyl and 26 kcal/mol for R = chloride.
- 2) In the modified Chalk-Harrod mechanism, the rate-determining step is the ethylene insertion into the Pt-SiCH<sub>3</sub> bond and its barrier is 44 kcal/mol for R = H and Me, and 60 kcal/mol for R = chloride.

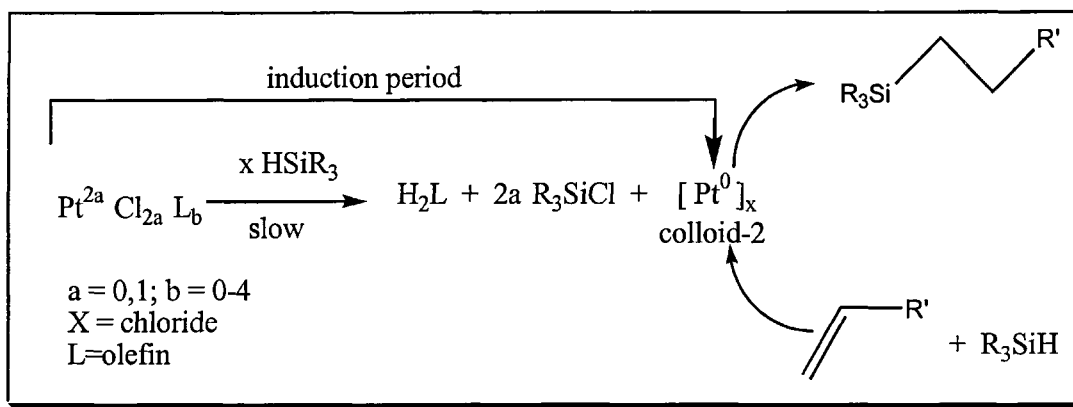
During the hydrosilylation, the platinum is converted from a very reactive monomeric (or dimeric) species into platinum colloids. The accompanying colour change (yellow brown → brown → black) is one of the problems of this reaction.

Variations on this mechanism have been proposed, the most significant of which was by Lewis in 1986, who showed that platinum-catalysed hydrosilylation proceeds with formation of platinum colloids<sup>128</sup>. The reaction of CODPtCl<sub>2</sub> (COD = 1,5-cyclooctadiene) with (EtO)<sub>3</sub>SiH suggests that colloid formation is the key step in hydrosilylation. Colloids are generated from the reactions of Pt(COD)<sub>2</sub> and CODPtCl<sub>2</sub> with hydrosilanes (Equation 2) and their formation precedes the hydrosilylation reaction.

**Equation 2:**

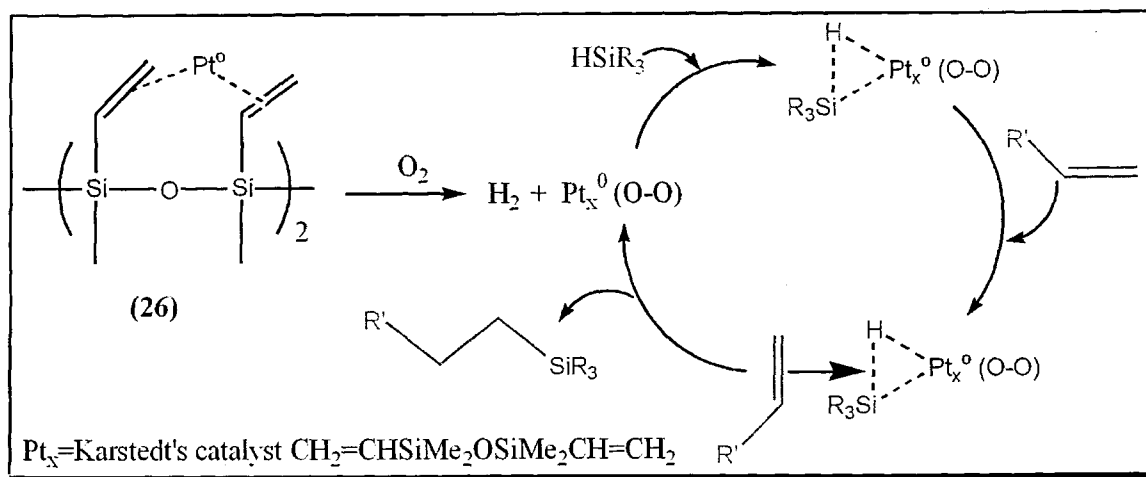


In the Lewis mechanism the active catalyst is the colloidal metal, as shown in Scheme 41. The reaction of  $\text{Me}_3\text{Si}(\text{CH}=\text{CH}_2)$  and  $(\text{EtO})_3\text{SiH}$  in the presence of  $(\text{COD})_2\text{Pt}$  is exothermic after a brief induction period at 25 °C and complete within about 15 min.



**Scheme 41: Formation of the colloid and hydrosilylation of the olefin.**

Similarly, the divinyltetramethyldisiloxane complex of  $\text{Pt}(0)$ , known as Karstedt's catalyst, has been shown to be a very active platinum hydrosilylation catalyst. This reaction requires the use of oxygen during the hydrosilylation reaction, since oxygen binds to the active catalyst species.



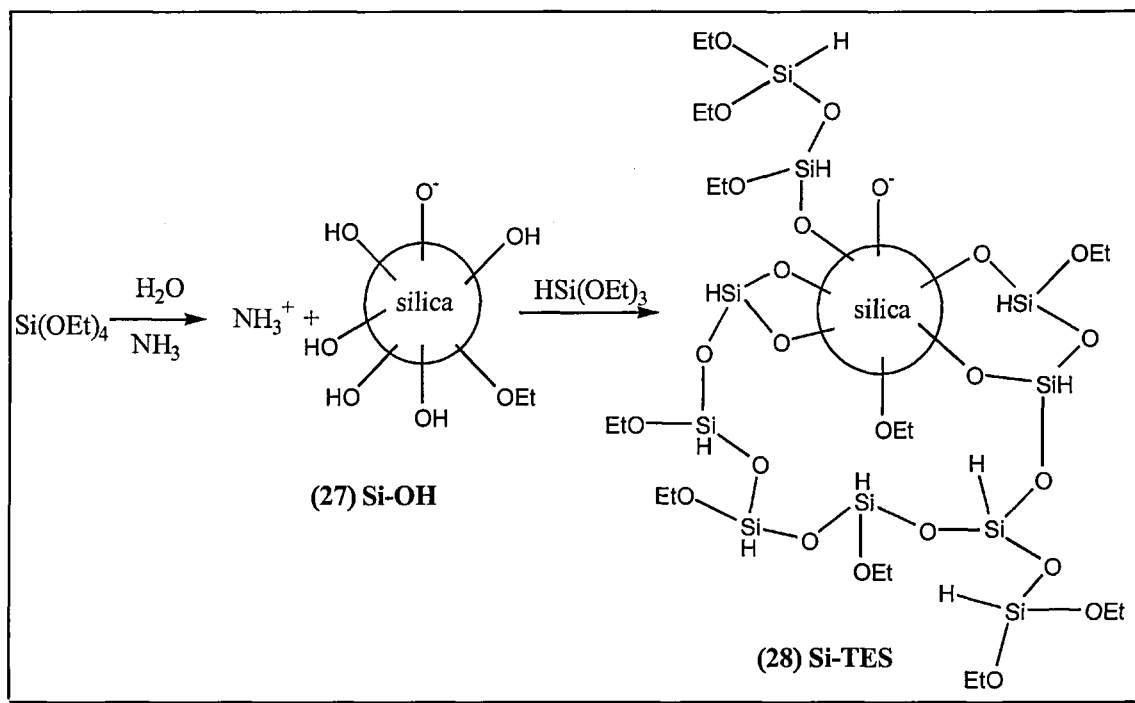
**Scheme 42: Hydrosilylation using Karstedt catalyst.**

This proposal, while controversial, accounted for the factors which are known to effect the reaction (*e.g.*, presence of colloids and the requirement of oxygen).

Investigations have demonstrated that exceptional care must be exercised to avoid larger colloid formation (*e.g.*, drying the sample, in particular, facilitates the formation of larger colloids) and that larger colloids are catalytically inactive. Minimising the formation of larger colloids appears to be an important part of maintaining catalytic activity and avoiding the colouration of the materials during the hydrosilylation reaction.

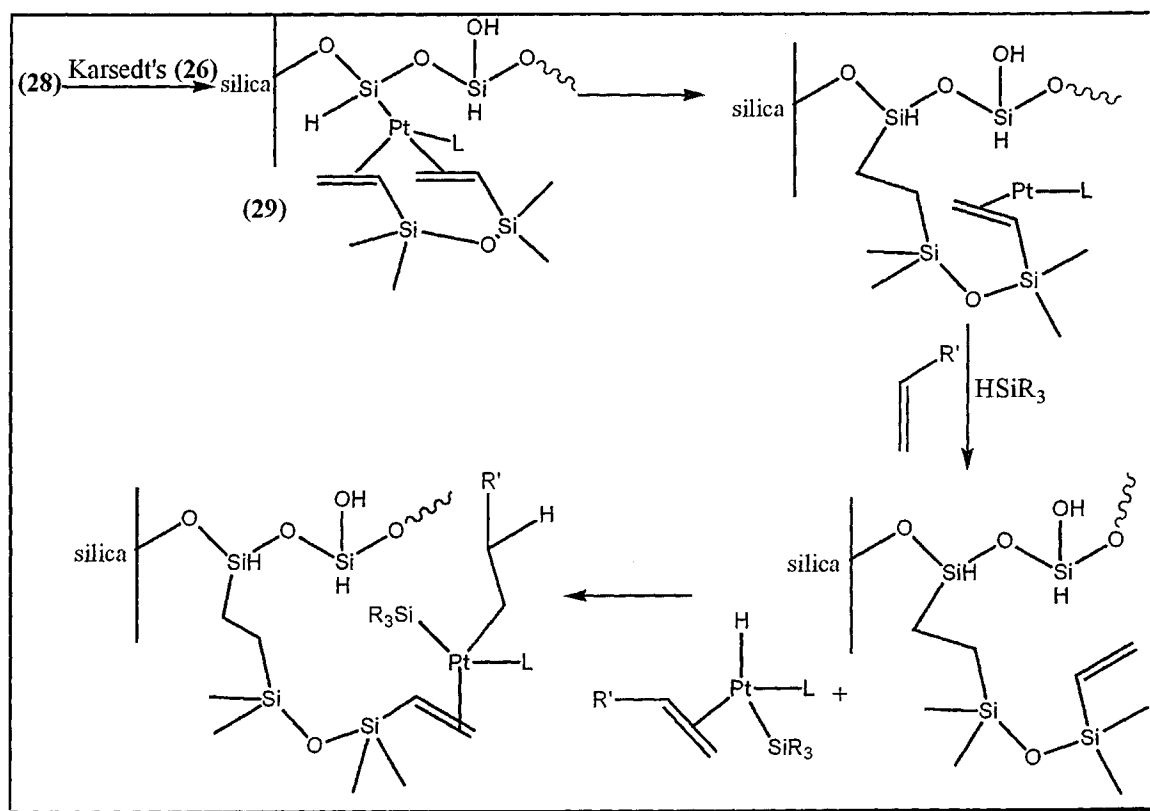
More recently, Brook and co-workers have described a platinum catalyst system which shows only limited platinum colloid formation, such that upon drying 2nm platinum particles were formed and larger colloids were not observed<sup>130, 131</sup>. Moreover, the catalytic system could be used for several hydrosilylation reactions without significant loss of the catalytic reactivity.

An alternative approach is the Stöber route, which involves the preparation of colloidal silica (**26**), followed by the binding of organosilanes to the silica surface. As shown in Scheme 43 this process involves the condensation of surface Si-OH groups with an alkoxy silane coupling agent, a modification performed in the absence of water (0.3 wt.% H<sub>2</sub>O measured by Karl-Fisher titration). Karstedt's catalyst solution was then added to this TES-modified silica (**28**) (TES = triethoxysilane). The opaque silica dispersion in THF turned a translucent yellow, and after drying the silica particles became grey in colour. The TEM shows 2nm platinum particles dispersed in the TES surface layer. Larger aggregates were not found, neither was platinum found away from the particle surface. The reaction of the catalyst with the TES surface leads to loss of all <sup>29</sup>Si NMR signals near 84.5 ppm which are associated with T<sup>H</sup> groups (RO<sub>3</sub>SiH); thus loss of the Si-H groups from the surface gives the active catalyst.



**Scheme 43: Formation of (27) Si-OH by the Stöber route and modifications of the silica surface to form (28) Si-TES.**

Suspensions of the Pt-TES-silica particles in THF have proven to be efficient catalysts in the hydrosilylation reaction (Scheme 44). As with normal hydrosilylations using Karstedt's catalyst alone, a yellow-orange coloured reaction solution is formed in solution. In fact, the silica particles become yellow during and after the reaction process, which show no agglomeration of the platinum. In the absence of extensive metal aggregation the catalyst can be recycled several times.



**Scheme 44: Formation of Si-TES-Pt (29), and the hydrosilylation reaction with this active catalyst.**

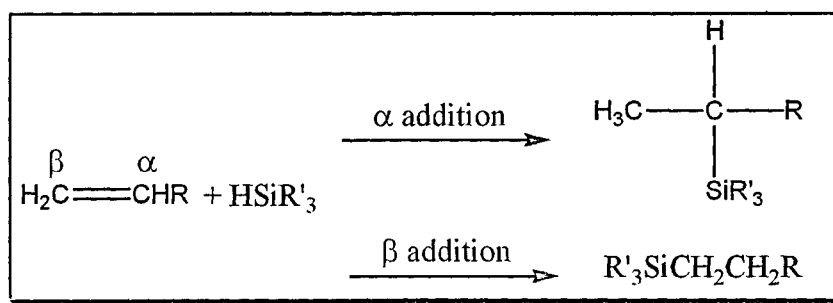
As discussed above, a great deal of work has been undertaken to understand the mechanism and behaviour of the hydrosilylation reaction. In all cases, it has been reported in the literature that hydrosilylation reactions are usually



accompanied by side reactions that reduce the yield of the desired product. The main side reactions are discussed in section 3.7.1, 3.7.2, 3.7.3 and 3.7.4<sup>127</sup>:

### 3.7.1-Two types of addition of the silane to the alkene: $\alpha$ and $\beta$ addition

Alkene compounds usually couple to silanes through hydrosilylation involving anti-Markovnikov addition. This is known as Farmers rule<sup>133</sup>. The  $\alpha$  and  $\beta$  adducts are shown in Scheme 45.

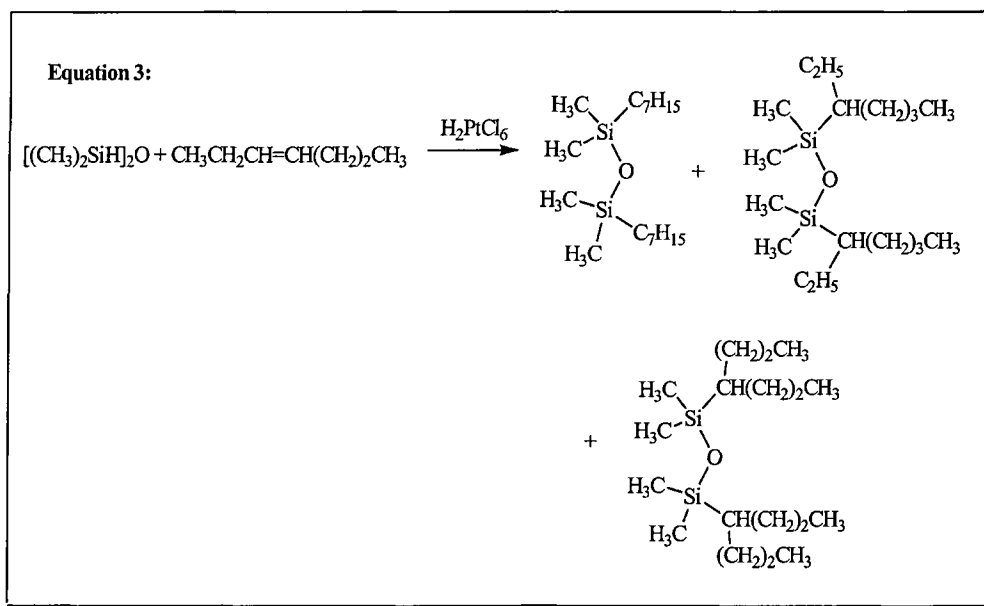


**Scheme 45:  $\alpha$  and  $\beta$  addition of the silane to the alkene by hydrosilylation**

This attachment of the silicon to the  $\beta$  carbon produces a straight chain alkane attached to the silicon species. Another addition involves the attachment of the silicon to the more substituted carbon of the vinyl group, the  $\alpha$  carbon. This involves the formation of a  $\text{CH}_3$  terminal group. The  $\beta$  addition is the main reaction but occasionally  $\alpha$  addition occurs to give the branch chain. Different factors change the ratio between the  $\alpha$ - and  $\beta$ - products, such as the solvent and the nature of the silane and alkene. These factors will be discussed in detail later in this literature survey.

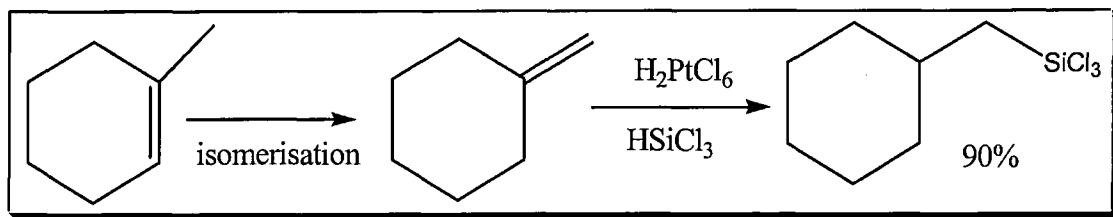
### 3.7.2-Alkene isomerisation.

Chlorosilicon hydrides in the presence of a platinum catalyst always add to linear olefins to give almost exclusively the primary alkylsilane. However, hydrosilylation of internal alkenes often involves isomerisation of the alkene. Speier and co-workers investigated hydrosilylations of 1,1,3,3-tetramethyldisiloxane (TMDS) with isomers of hexene<sup>136</sup>. Hex-1-ene produced the expected 1-hexyl product, however, hex-2-ene and hex-3-ene provided a mixture of isomers owing to alkene isomerisation. In the presence of chloroplatinic acid, TMDS and hept-3-ene formed 1-, 3-, 4- *n*-heptyltetramethyldisiloxane compounds, as shown in equation 3.



In some cases this alkene isomerisation is welcome as they give products that are difficult to synthesise. Internal double bonds are less reactive than terminal alkenes, so when an isomerisation takes place, the thermodynamically less

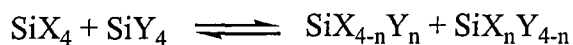
stable terminal alkene undergoes hydrosilylation reasonably quickly and results in the terminal isomer being the major product, as shown in Scheme 46.



**Scheme 46: Isomerisation of an alkene and hydrosilylation by a trichlorosilane using chloroplatinic acid as catalyst.**

### 3.7.3-Polymerisation of the hydrosiloxane<sup>135-138</sup>.

Redistribution constitutes an important class of reaction in organosilicon chemistry. The reaction is shown below, where one or more substituents X and Y are exchanged.



**Scheme 47**

Redistribution of the group on silicon can be initiated by thermolysis or by catalytic activation using catalysts such as strong bases, strong protic or Lewis acids or transition metal complexes (such as chloroplatinic acid). Thus redistribution can be a problem in hydrosilylation giving products with a high molecular weight.

### 3.7.4-Metal catalysed cleavage of the Si-C bond<sup>137-140</sup>.

The Si-C bonds formed by hydrosilylation of  $\alpha,\beta$ -unsaturated compounds can be broken by protic and aprotic acids, halogens and nucleophiles or transition metals. A wide range of platinum and palladium complexes brings about the removal of unsaturated groups from the silicon group.

### 3.8-Studies of the $\alpha/\beta$ ratio in the hydrosilylation of olefins using different conditions.

A number of studies have been carried out in order to investigate the factors affecting the  $\alpha/\beta$  ratio in the hydrosilylation of olefins. This  $\alpha/\beta$  ratio has been shown to depend on a number of different parameters such as the substrate structure, the nature or concentration of the catalyst and the solvent. This survey will list the major types of hydrosilylation reactions reported in the literature and show the variety of compounds that have been hydrosilylated and the wide range of  $\alpha/\beta$  ratios obtained in the products.

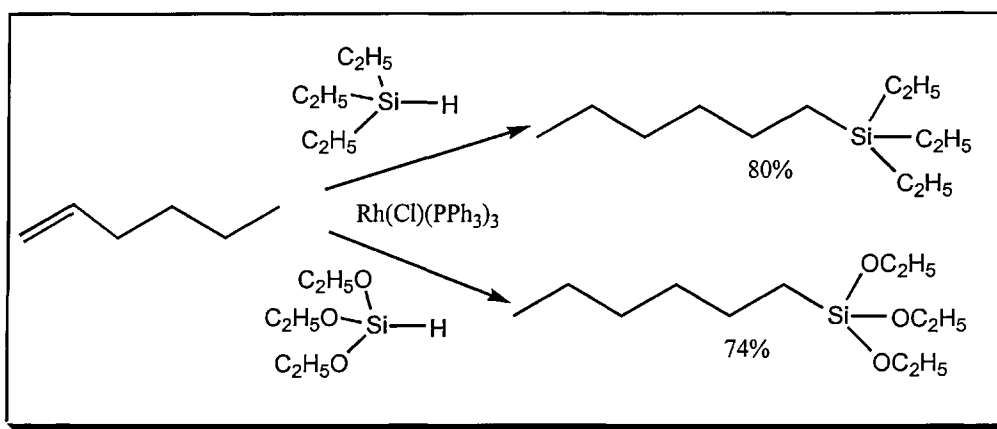
#### 3.8.1-Hydrosilylation of alkenes.

##### 3.8.1.1-Hydrosilylation of 1-alkenes.

Hex-1-ene was hydrosilylated with different silanes to give in most cases  $\beta$ -addition. No difference in yield or time of reaction was observed when using triethylsilane or triethoxysilane, which proved that the nature of the silane did not affect the outcome of the reaction<sup>141</sup>. Hydrosilylations of hex-1-ene with two different platinum catalysts, chloroplatinic acid and a platinum

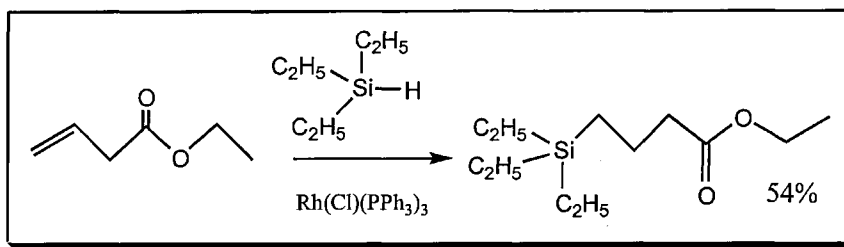
cyclovinylmethylsiloxane complex, were reported to yield anti-Markovnikov substituted di-n-alkyldichlorosilanes<sup>142</sup>.

Chalk reacted hex-1-ene with triethylsilane and reported an 80 % yield of the  $\beta$  product using  $\text{RhCl}(\text{PPh}_3)_3$  as catalyst. Using triethoxysilane in the same hydrosilylation gave the same  $\beta$  product in 74 % yield<sup>143</sup>. In 1982, hydrosilylation of hex-1-ene with triethoxysilane using Wilkinson's catalyst derivatives, such as rhodium (I) complexes with phosphino-alkyl organosilicon ligands, yielded 80 % to 58 % of the  $\beta$ - product hexyltriethoxysilane, depending of the silane used<sup>142</sup>, as shown in Scheme 48.



**Scheme 48: Hydrosilylations of hex-1-ene**

Recently, the hydrosilylation of methyl 3,3-dimethylpent-4-enoate with dimethylchlorosilane in the presence of a dichloro(1,5-cyclooctadiene)platinum(II) catalyst was reported to give dimethylsilyl 4-pentenoate<sup>147</sup>. Furthermore the yield of  $\beta$ -addition product was 84 % with 3-methyl-4-penten-2-one and dimethylchlorosilane<sup>146</sup> and 54 % with ethyl butenoate and triethylsilane<sup>147</sup>, as presented in Scheme 49. In all cases no  $\alpha$ -addition was reported.

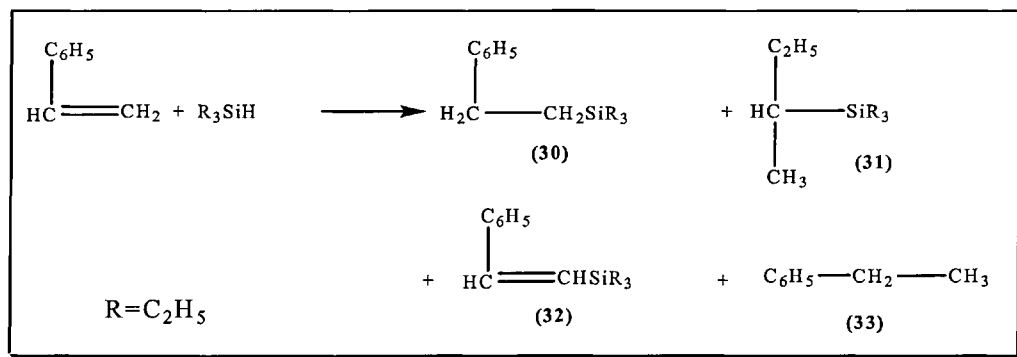


**Scheme 49: Hydrosilylation of ethylbutenoate using triethylsilane**

### 3.8.1.2-Hydrosilylation of styrene

The addition of trichlorosilane to styrene, at atmospheric pressure, in the presence of a solution of chloroplatinic acid in 2-propanol as catalyst resulted in 100 %  $\beta$ -addition in 25 to 60 % yields<sup>148</sup>.

Hydrosilylation of styrene in the presence of  $\text{PtCl}_2$  catalysts has been carried out using triethylsilane, as shown in Scheme 50<sup>149</sup>. This reaction not only the saturated hydrosilylated products (30) and (31) in 74 % and 4 % yield respectively, but also, after 4 h, the unsaturated (32) and hydrogenated products (33) both in 11 % yield.



**Scheme 50: Hydrosilylation of styrene**

When using triphenylsilane the reaction is slower, and the product was only formed after 96 h. However, it is regiospecific, giving only the linear

regioisomer (30) and the side products (32) and (33). This phenomenon has also been reported in previous work<sup>150</sup>.

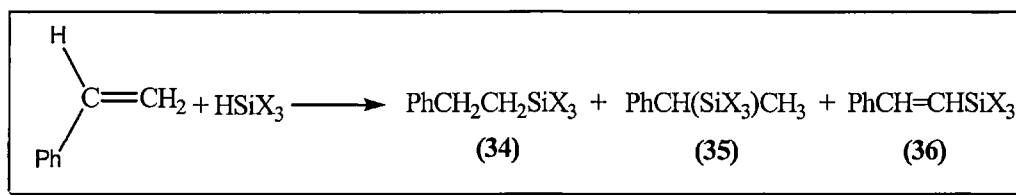
Trimethylsilane and phenyldimethylsilane have been used in the presence of  $\text{PtCl}_2$  for the hydrosilylation of styrene providing both isomers in a ratio of  $\alpha/\beta = 2:76$ .

Similarly Foldes reported the reactions of styrene with different alkylsilanes using a variety of catalysts<sup>151</sup>. For example, addition of methyldichlorosilane to styrene catalysed by nickel complexes gave the products (30) and (31) in 24 % yield combined. The  $\alpha/\beta$  ratio is 46:54. Addition of trimethylsilane or phenyldimethylsilane in the presence of a rhodium catalyst gives the 2-adduct (31), and the 1-adduct (30), with an  $\alpha/\beta$  ratio 30:70.

Other catalysts give different ratios, the diplatinum complexes  $[\{\text{Pt}(\text{SiR}_3)(\mu\text{-H})(\text{C}_6\text{H}_{11})\text{P}\}_2]$  gave only the  $\beta$  adduct, except when using dimethylchlorosilane, in which case 78 % of the  $\beta$  adduct and 22 % of the  $\alpha$  adduct were observed<sup>152</sup>.

The two component Ziegler catalyst  $[\text{Rh}(\text{acac})_3]\text{-AlEt}_3$  and its analogues have been investigated by Lappert *et al* for the hydrosilylation of styrene at  $60\text{ }^\circ\text{C}$ <sup>153</sup>.

The products are presented in Scheme 51.



**Scheme 51: Hydrosilylation of styrene**

Using alkylsilanes, the dehydrogenated hydrosilylated material, the vinylsilane (36)  $\text{PhCH}=\text{CHSiX}_3$  (X = ethyl, phenyl or O-ethyl), was the principal product

(yield = 80 %), with isomeric 1/1 adducts as by-products. The terminal adduct  $\text{Ph}(\text{CH}_2)_2\text{SiX}_3$  (**34**) was obtained in 12 % yield.

Alkoxysilanes however gave the terminal adduct (**34**) as the major product (yield = 45 %) and  $\text{PhCH}_2\text{CH}(\text{SiX}_3)\text{CH}_3$  (**35**) ( yield = 6 %) and  $\text{PhCH}_2\text{CH}=\text{CHSiX}_3$  (**36**) (yield =15 %) in smaller proportions.

The effect of solvent was also studied on the  $\alpha/\beta$  ratio of products obtained during the hydrosilylation. For styrene, Musolf and Speier have shown that the addition of 2 % by volume of tetrahydrofuran (with respect to the olefin) in the reaction with trichlorosilane led exclusively to the 2-adduct, while in the case of the methyldichlorosilane both isomers were formed with an  $\alpha/\beta$  ratio of 19/81<sup>154</sup>.

### 3.8.2-Hydrosilylation of alkenyl ethers.

#### 3.8.2.1-Hydrosilylation of allyl butyl ether.

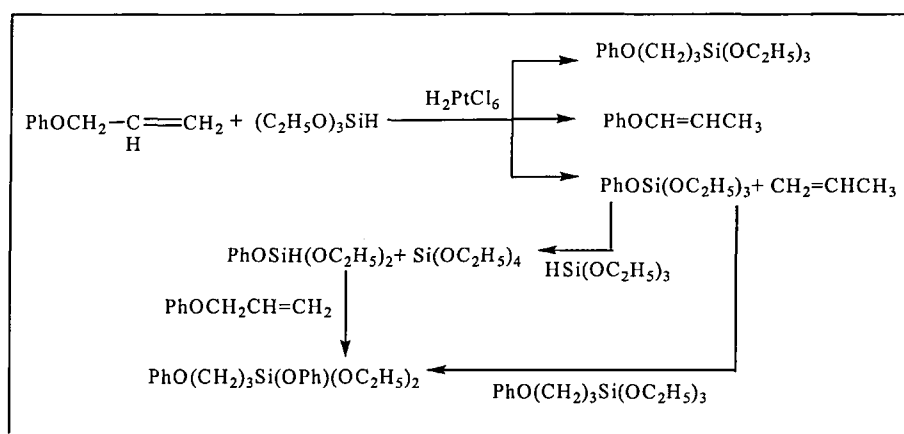
Eaborn used chloroplatinic acid to catalyse the hydrosilylation of allyl butyl ether with benzyldimethylsilane to give 48 % of the  $\beta$ -product by distillation<sup>155</sup>.

Triethoxysilane gave only the  $\beta$ -addition product when using a platinum catalyst. In all cases no  $\alpha$ -addition was observed<sup>156-157</sup>. Murai examined the hydrosilylation of allyl butyl ether with trimethylsilane using cobalt  $\text{Co}_2(\text{CO})_8$  as the catalyst. The reaction gave 9 % of the  $\alpha$ - regioisomer although the  $\beta$ - addition product was not separated from the byproducts<sup>158</sup>.

#### 3.8.2.2-Hydrosilylation of allyl phenyl ether.



Hydrosilylation of allylphenyl ether and *ortho*-substituted allyl phenyl ethers in the presence of chloroplatinic acid has been studied in detail<sup>159</sup>. The reaction with triethoxysilane showed that, apart from the addition product and starting material, the reaction mixture contained about 25 % of unexpected compounds as impurities. One of these compounds proved to be the phenyl propenyl ether. The presence of this compound indicates the isomerization of allyl phenyl ether during the hydrosilylation. Scheme 52 shows the different products obtained:

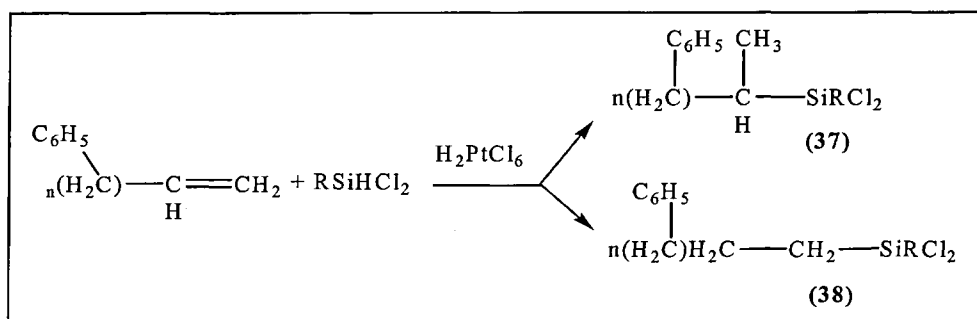


**Scheme 52: Hydrosilylation and isomerization of allylphenyl**

### 3.8.3-Hydrosilylation of allylbenzene.

Preparation of  $\text{R}_x\text{Cl}_{3-x}\text{Si}(\text{CH}_2)_n\text{C}_6\text{H}_5$  (with  $n = 2$  or more) was studied by Petrov in 1960 *via* the addition of a hydrosilane to allylbenzene using a catalytic amount of chloroplatinic acid<sup>160</sup>. When using trichlorosilane, the hydrosilylation product is solely the  $\beta$ -adduct. The addition of methyldichlorosilane and ethyldichlorosilane to allylbenzene gave a 56 % yield of the two isomers (37) and (38), as shown in Scheme 53.

Four to six times as much of the isomer **(38)** was formed, compared to the isomer **(37)**. When  $n = 0$  the  $\beta/\alpha$  ratio is 68:32.

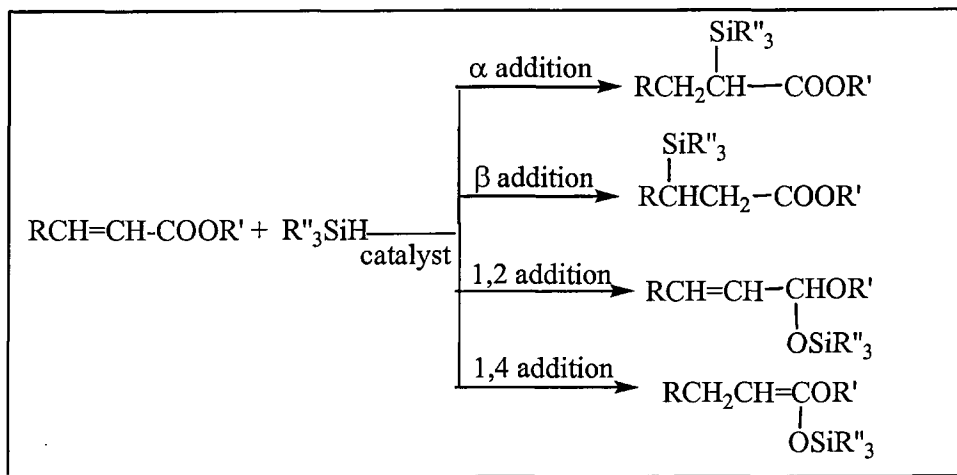


**Scheme 53: Hydrosilylation of allylbenzene**

Hydrosilylation of allylbenzene in the presence of  $[\text{Rh}(\text{acac})_3]\text{Al}(\text{C}_2\text{H}_5)_3$  showed similar results to those found for styrene, only with a much smaller proportion of the substituted olefin  $\text{PhCH}=\text{CHSi}(\text{C}_2\text{H}_5)_3$  (**26**); in 7 % yield with the alkoxy-silane and 15 % yield with the alkylsilane.

#### 3.8.4-Hydrosilylation of an $\alpha/\beta$ unsaturated ester.

The hydrosilylation of  $\alpha,\beta$ -unsaturated esters using different catalysts gave rather complex results. The selectivity was dramatically affected by the substituent on the ester group and that on the  $\beta$  carbon<sup>163</sup>. The reaction gives four possible products as shown in the Scheme 54, namely, the  $\alpha$ - and  $\beta$ -adducts from the 1,2 addition to the  $\text{C}=\text{C}$  bond, the adduct from the 1,2 addition to the carbonyl group and the 1,4 adduct.



**Scheme 54: The four possible products from the hydrosilylation of  $\alpha,\beta$  unsaturated esters.**

The hydrosilylation of hexyl acrylate using chloroplatinic acid has been studied by Ojima, who has shown that the outcome of the reaction depends on the nature of the silane<sup>162</sup>.

Chlorosilanes gave a mixture of  $\alpha$ -,  $\beta$ - and 1,4-addition products, whereas triethylsilane afforded exclusively the  $\beta$ -product.

### 3.8.5-Hydrosilylation of but-3-enoic acid.

The reduction of carboxylic acids to aldehydes using hydrosilanes has been reported by Corriu<sup>163, 164</sup>. But-3-enoic acid reacted in two ways with triethylsilane, giving the  $\alpha$ -adduct  $(C_2H_5)_3Si(CH_2)_3COOH$  or the oxysilylation product  $(C_2H_5)_3SiOCO(CH_2)_3Si(C_2H_5)_3$ . A similar result has been obtained using triethoxysilane.

### 3.8.6-Conclusions.

Whilst a number of publications has shown how the  $\alpha/\beta$  ratio varies on changing the conditions, and many factors have been suggested to be important, the exact mechanistic rationale for the different amounts of  $\alpha$  and  $\beta$  adducts has not been discussed in detail in the literature.

In our study, we compare the  $\alpha/\beta$  ratio for the hydrosilylation of olefins in the presence of platinum catalysts (chloroplatinic acid or Karstedt catalyst), using triethylsilane or triethoxysilane, and varying the solvent from a “normal” organic solvent (tetrahydrofuran) to ionic liquids.

# Chapter 4

## **Chapter 4-Results and Discussion of hydrosilylation of alkenes in ionic liquids.**

Ionic liquids have been found to be environmentally friendly solvents and more recently have been found to have interesting effects on catalytic reactions. In the initial chapters we have discussed how the reduction of aldehydes in organic solvent can be achieved using nucleophiles as promoters and silanes as reducing agents. One of the problems that arises in this reduction is the presence of the ionic salt in the mixture, and in particular the fact that tetrabutylammonium salts are difficult to remove from the mixture at the end of the reaction. The removal of salt is achieved by successive washing and leads to loss of the products. The use of ionic liquids as solvents in this reaction has many advantages:

- they are liquid over a wide range of temperatures ( $-70^{\circ}\text{C}$  to more than  $400^{\circ}\text{C}$ )
- they are non volatile
- there is a large array of ionic liquids with different cations and anions
- they can be used both as solvent and catalyst. In the reduction of aldehydes they are a good source of nucleophiles
- they permit a two-phase reaction, which allows an easy separation of the products at the end of the reaction
- they are recyclable and reusable

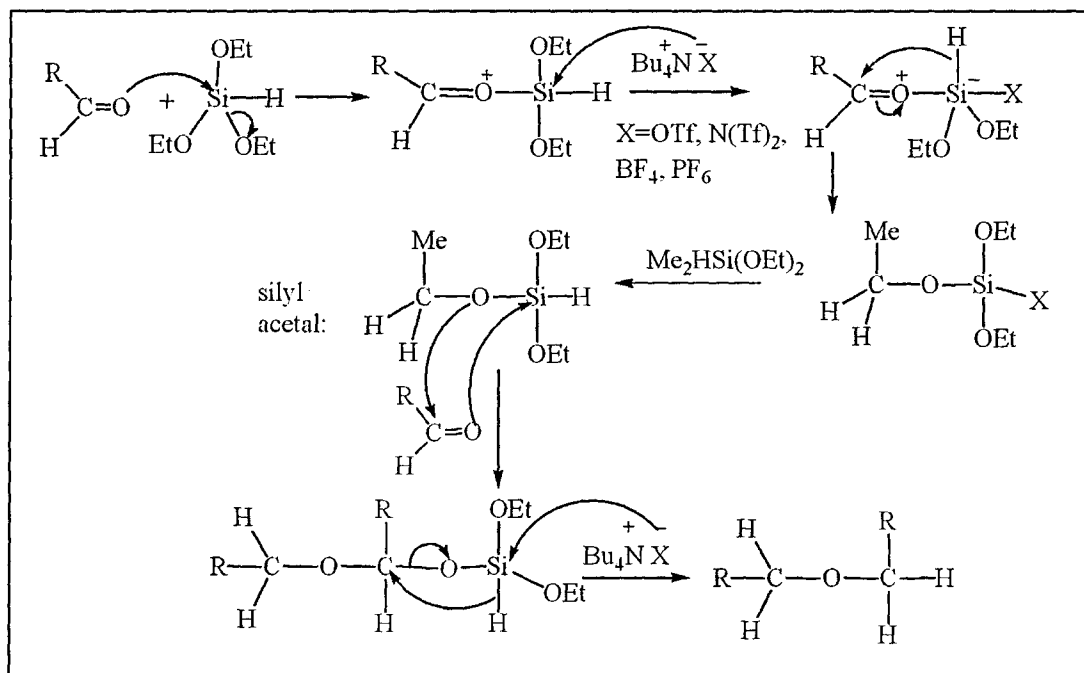
Four types of ionic liquids have been prepared in our laboratory and used to catalyse the reduction of aldehydes *via* hydrosilylation. We have also studied the hydrosilylation of alkenes in ionic liquids in the presence of transition metals catalysts and others types of silicon-based reactions. This study will provide more insight into how a change of solvent affects the outcome of hydrosilylation and other silicon based reactions.

#### **4.1-Reduction of aldehydes with $\text{HSi}(\text{EtO})_3$ and $\text{Me}_2\text{HSiCl}$ in ionic liquids.**

1-Butyl-3-methylimidazolium triflate [bmim][OTf], tetrafluoroborate [bmim][BF<sub>4</sub>], hexafluoroborate [bmim][PF<sub>6</sub>] and [bmim][NTf<sub>2</sub>] were used as solvents and as sources of anion for the reduction of a series of aldehydes in the presence of  $\text{HSi}(\text{EtO})_3$  and  $\text{Me}_2\text{HSiCl}$  as reducing agents.

##### **4.1.1-Reduction of benzaldehyde.**

Whilst the benzaldehyde dissolved in the ionic liquid the silane formed a separate organic phase. The reaction therefore occurred at the interface. In order to ensure intimate interaction between the two reagents it is very important to stir well. The mechanism of the reaction is the same as in the presence of salts except that the nucleophile is the anion of the ionic liquid which promotes the reaction, as shown in Scheme 55.



**Scheme 55: Reduction of aldehydes with triethoxysilane in ionic liquids.**

The anion of the ionic liquid attacks the silicon and thus forms a pentacoordinate silicon species where the Si-H bond is activated. The benzaldehyde is reduced to give a symmetric dibenzyl ether, which is isolated by distillation. In this reaction an excess of silane is needed; therefore, we used 2.5 equivalents compared to the aldehyde. Furthermore, some silanes react more readily with the small amount of water present in the ionic liquids.  $^1\text{H}$  NMR spectroscopy confirmed the formation of the dibenzyl ether showing a single signal at 3.44 ppm corresponding to the  $\text{CH}_2$  protons next to an oxygen atom, and the  $^{13}\text{C}$  NMR spectroscopy showed a signal at 72.1 ppm. This reduction was only observed for two ionic liquids, [bmim][OTf] and [bmim][NTf<sub>2</sub>]. With the two other ionic liquids, [bmim][PF<sub>6</sub>] and [bmim][BF<sub>4</sub>], the NMR only contained signal corresponding to the starting materials: triethoxysilane in the organic phase and benzaldehyde in the ionic liquid phase.



The isolated yields of the dibenzyl ether obtained with [bmim][OTf] when using (EtO)<sub>3</sub>SiH or Me<sub>2</sub>HSiCl were, respectively, 72 % and 69 %. This shows the effectiveness of both silanes in the reduction reaction and reinforces the preference for the triethoxysilane compared to the dimethylchlorosilane. The yields of the dibenzyl ether obtained using (EtO)<sub>3</sub>SiH or Me<sub>2</sub>HSiCl in [bmim][NTf<sub>2</sub>] were 61 % and 59 %, respectively. Comparing this with the yields obtained in [bmim][OTf] suggests that the reduction reaction occurred more readily in [bmim][OTf] than in [bmim][NTf<sub>2</sub>]. This is may be due to the ability of the anion of the ionic liquid to attack the silicon atom and form a pentacoordinate silicon species. The relative nucleophilicity for the attack of the anion of the ionic liquid at the silicon atom is [OTf] > [NTf<sub>2</sub>] > [BF<sub>4</sub>] or [PF<sub>6</sub>]. This result is not surprising since oxygen-silicon bonds are easier to form than nitrogen silicon bonds and are both easier to form than boron-silicon or phosphorus-silicon bonds.

If we now compare the isolated yields of dibenzyl ether obtained in ionic liquids (72-59 %) with those calculated by GC using the salts (70-43 %), we notice a general improvement when using an ionic liquid as the solvent and source of the nucleophile. This result might be influenced by a range of factors, such as the easier separation of reagents and products, the higher concentration of anions in the reaction mixture and the favourable reaction in non-volatile and very polar solvents such as ionic liquids.

If we leave the reactions longer and under reflux, the yields are similar; thus, the simplest conditions for the reduction reaction (room temperature and good stirring) seems to give the best yield.

#### 4.1.2-Reduction of butanal

Butanal was also reduced by both of the silanes in [bmim][OTf] and [bmim][NTf<sub>2</sub>]; the reduction reaction gave dibutyl ether in 90-77 % isolated yield. This reaction was visibly very exothermic since, on addition of the silane, there is an increase of temperature and a change in colour, from colourless to yellow. Again the yield of the ether obtained depends upon the silane and ionic liquid used. No reaction was observed using [bmim][BF<sub>4</sub>] and [bmim][PF<sub>6</sub>] as the solvent and the source of anion. We generally obtained a better yield of the ether with the reduction of butanal than with the benzaldehyde.

#### 4.1.3-Reduction of octanal.

Octanal reacted with silanes in [bmim][OTf] and [bmim][NTf<sub>2</sub>] to give dioctyl ether in 75-62 % isolated yield after 2 h at room temperature. Comparing these results with butanal, we see that the reduction of butanal gives a higher yield than octanal. This is in line with the results obtained when reacting butanal with dimethylchlorosilane in the presence of tetrabutylammonium chloride or triflate salts giving 58 % and 35 % isolated yield, respectively, compared with the reduction of octanal by the same silane and salts which gave lower yields of 39 % and 29 % isolated yield, respectively. The difference in yields when using butanal compared with octanal is 15-20 % with either the salt or the ionic liquid. Leaving the reaction longer and under reflux did not improve the yield, and the unreacted aldehyde remained in the ionic liquid phase. After addition of the silane the reaction did change colour to provide a salmon coloured reaction mixture.

#### 4.1.4-Reduction of trimethylacetaldehyde.

The reduction of trimethylacetaldehyde with  $\text{Me}_2\text{HSiCl}$  in  $[\text{bmim}][\text{OTf}]$  gave di-(2,2-dimethylpropyl) ether in 49 % isolated yield and in  $[\text{bmim}][\text{NTf}_2]$  gave 45 %-isolated yield. The  $^1\text{H}$  NMR spectrum shows a single signal at 3.7 ppm corresponding to two  $\text{OCH}_2$  protons and the  $^{13}\text{C}$  NMR spectrum shows a signal at 83.5 ppm corresponding to the  $\text{OCH}_2$  carbon in the ether.

Trimethylacetaldehyde is reduced in ionic liquids but in a lower yield compare to other aldehydes. This is due to the steric effect which slows down the attack of the aldehyde at the silicon atom. However, the yields obtained in ionic liquids are better than those obtained for the salts (38-22 %).

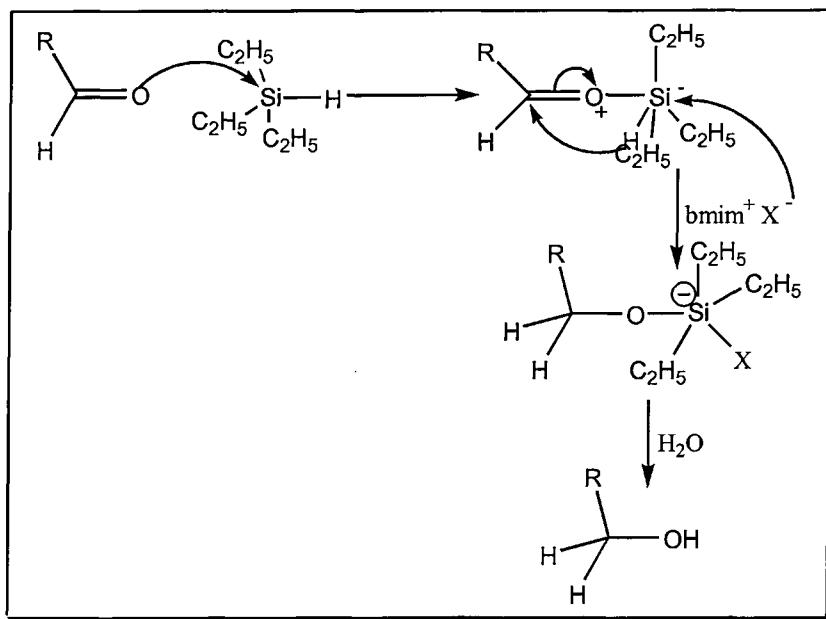
#### 4.2-Reduction of aldehydes with $\text{HSi}(\text{Et})_3$ in ionic liquids.

The four ionic liquids were also used for the reduction of aldehydes using triethylsilane. As we saw in the Chapter 1, Section 1.4.1.2, triethylsilane is one of the less efficient reducing agents in the reduction reactions using salts (reference 24). However, the change to a polar and non volatile solvent could promote the efficiency of the triethylsilane, depending on the solubility of the silane in the ionic liquids.

##### 4.2.1-Reduction of benzaldehyde.

Benzaldehyde is reduced by  $(\text{Et})_3\text{SiH}$  in the ionic liquids to give the corresponding alcohol in 50 %-44 % yield. The  $^1\text{H}$  NMR spectrum confirmed the presence of the OH, showing a signal at 2.58 ppm. Triethylsilane is less reactive than triethoxysilane and dimethylchlorosilane and did not lead to the

formation of the ether in this reduction reaction. The mechanism involved in this reaction is described in Scheme 56:



**Scheme 56: Hydrosilylation of aldehydes with triethylsilane in ionic liquids.**

The oxygen of the carbonyl group of the benzaldehyde attacks the silicon atom and forms the pentacoordinated species. The triethyl groups are not good leaving groups and stay attached to the silicon atom. The anion of the ionic liquid attacks the silicon atom promoting the hydrogen transfer from the silicon atom to the carbon of the carbonyl group. After hydrolysis, the product was the corresponding alcohol which dissolved in the ionic liquid and had to be isolated by distillation.

#### 4.2.2-Reduction of butanal.

Butanal is also reduced in ionic liquids by triethylsilane and gave the corresponding butanol in 65 %-60 % yield. If we compare this with the

reduction of benzaldehyde we see that the butanal gave a better yield of alcohol than the benzaldehyde.

#### 4.2.3-Reduction of trimethylacetaldehyde.

The  $^1\text{H}$  NMR spectrum of the product from the reaction of triethylsilane with trimethylacetaldehyde showed a triplet at 2.2 ppm with an integration equal to one hydrogen corresponding to the OH and a doublet at 3.52 ppm with an integration equal to two hydrogen, corresponding to the  $\text{CH}_2$  next to the OH. These signals have a coupling constant equal to  $^3J = 7 \text{ Hz}$ . This suggests the formation of 2,2-dimethylpropanol in the reduction reaction in 37 %-31 % isolated yield.

The  $^{13}\text{C}$  NMR spectrum confirmed this analysis showing a signal at 67.54 ppm which is due to the carbon next to the OH.

#### 4.2.4 Summary and conclusions.

The reduction of aldehydes in ionic liquids occurs at room temperature with triethoxysilane, dimethylchlorosilane and triethylsilane. The results depend on the nature of the ionic liquids, the nature of the silane and the different aldehydes used. Two of the four ionic liquids promote the reaction:

[bmim][OTf] and [bmim][NTf<sub>2</sub>] did not activate the silicon-hydrogen bond for a hydride transfer.

Triethoxysilane and dimethylchlorosilane reduce the aldehydes to the ether in high yield. The yields are better than when salts were used as promoters, probably due to the easier separation of the products and reagents. When

triethylsilane was used the product obtained was the corresponding alcohol and the reaction is slower and less violent. In all cases, leaving the reaction longer or under reflux did not improve the yields. The different yields obtained are summarised in Table 49:

<b>(CH<sub>3</sub>CH<sub>2</sub>O)<sub>3</sub>SiH</b>				
<b>RCHO R =</b>	<b>C<sub>6</sub>H<sub>5</sub></b>	<b>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub></b>	<b>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub></b>	<b>C(CH<sub>3</sub>)<sub>3</sub></b>
bmim <sup>+</sup> OTf <sup>-</sup>	72% (1.34 g)	90% (1.61 g)	75% (1.4 g)	58% (1.06 g)
bmim <sup>+</sup> NTf <sub>2</sub> <sup>-</sup>	69% (1.28 g)	85% (1.53 g)	71% (1.35 g)	55% (1 g)
bmim <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	0	0	0	0
bmim <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	0	0	0	0
<b>(CH<sub>3</sub>)<sub>2</sub>HSiCl</b>				
<b>RCHO R =</b>	<b>C<sub>6</sub>H<sub>5</sub></b>	<b>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub></b>	<b>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub></b>	<b>C(CH<sub>3</sub>)<sub>3</sub></b>
bmim <sup>+</sup> OTf <sup>-</sup>	61% (1.43 g)	80% (1.5 g)	65% (1.2 g)	49% (0.9 g)
bmim <sup>+</sup> NTf <sub>2</sub> <sup>-</sup>	59% (1.1 g)	77% (1.38 g)	62% (1.16 g)	45% (0.83 g)
<b>(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>SiH</b>				
<b>RCHO R =</b>	<b>C<sub>6</sub>H<sub>5</sub></b>	<b>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub></b>	<b>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub></b>	<b>C(CH<sub>3</sub>)<sub>3</sub></b>
bmim <sup>+</sup> OTf <sup>-</sup>	50% (0.25 g)	65% (0.3 g)	52% (0.26 g)	37% (0.35 g)
bmim <sup>+</sup> NTf <sub>2</sub> <sup>-</sup>	44% (0.21 g)	60% (0.27 g)	49% (0.25 g)	31% (0.29 g)

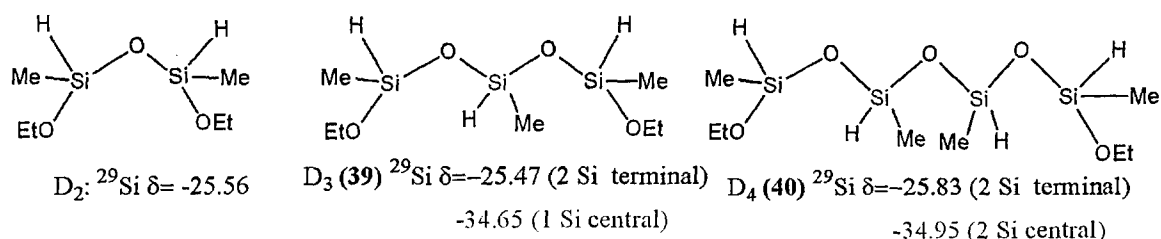
**Table 49: Isolated yield of ethers obtained in the reduction of aldehydes with silanes in ionic liquids**

#### 4.3-Reaction of silanes in ionic liquids in the absence of aldehydes.

The use of ionic liquids as solvents allows the easy separation of products and reagents. Alkoxysilanes undergo hydrolysis/condensation with water to give silanols and disiloxanes. Thus, we have been able to study the rearrangement of the alkoxysilanes in ionic liquids based on the trace amount of water present. Silanes were reacted with ionic liquids and then analysed by <sup>1</sup>H, <sup>13</sup>C NMR and, more importantly, <sup>29</sup>Si NMR spectroscopy.

#### 4.3.1-Hydrolysis/condensation reaction of MeHSi(OEt)<sub>2</sub> in [bmim][OTf] or [bmim][NTf<sub>2</sub>].

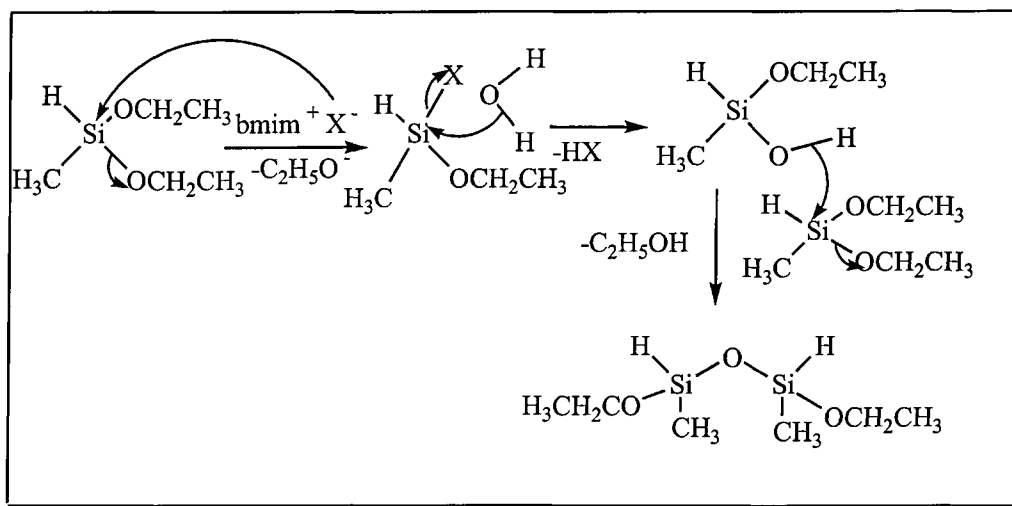
Two different ionic liquids were used as the solvent and source of nucleophiles in this reaction. We had observed in the reduction reaction that only [bmim][OTf] and [bmim][NTf<sub>2</sub>] could attack the silane to give an intermediate pentacoordinate silicon species. We thus assumed that the hydrolysis/condensation of the alkoxy silane would only proceed in these two ionic liquids. MeHSi(OEt)<sub>2</sub> was stirred at 60 °C in [bmim][OTf] or [bmim][NTf<sub>2</sub>] to give a mixture of linear siloxanes, as shown in Figure 13:



**Figure 13: Linear D<sub>2</sub>, D<sub>3</sub>, D<sub>4</sub> siloxanes obtained by reacting MeHSi(OEt)<sub>2</sub> with ionic liquids**

The three siloxanes have been analysed by  $^{29}\text{Si}$  NMR spectroscopy, where each silicon atom will have a different chemical shift depending on its environment. The disiloxane is a D<sub>2</sub>, since both silicon atoms are attached to two oxygen atoms (D). The two silicon atoms have the same environment so the  $^{29}\text{Si}$  NMR spectroscopy shows one signal at  $-25.56$  ppm. D<sub>3</sub> was also obtained and gave two signals in  $^{29}\text{Si}$  NMR spectroscopy at  $-25.47$  ppm and  $-34.65$  ppm with a ratio 2:1 corresponding to the two terminal silicon atoms (surrounded by one oxygen OEt and one oxygen Si-O-Si) and one central silicon atom with an O-Si-O as environment respectively. The D<sub>4</sub> showed two signals in the  $^{29}\text{Si}$  NMR spectroscopy with the same ratio belonging to the two terminal silicon atoms

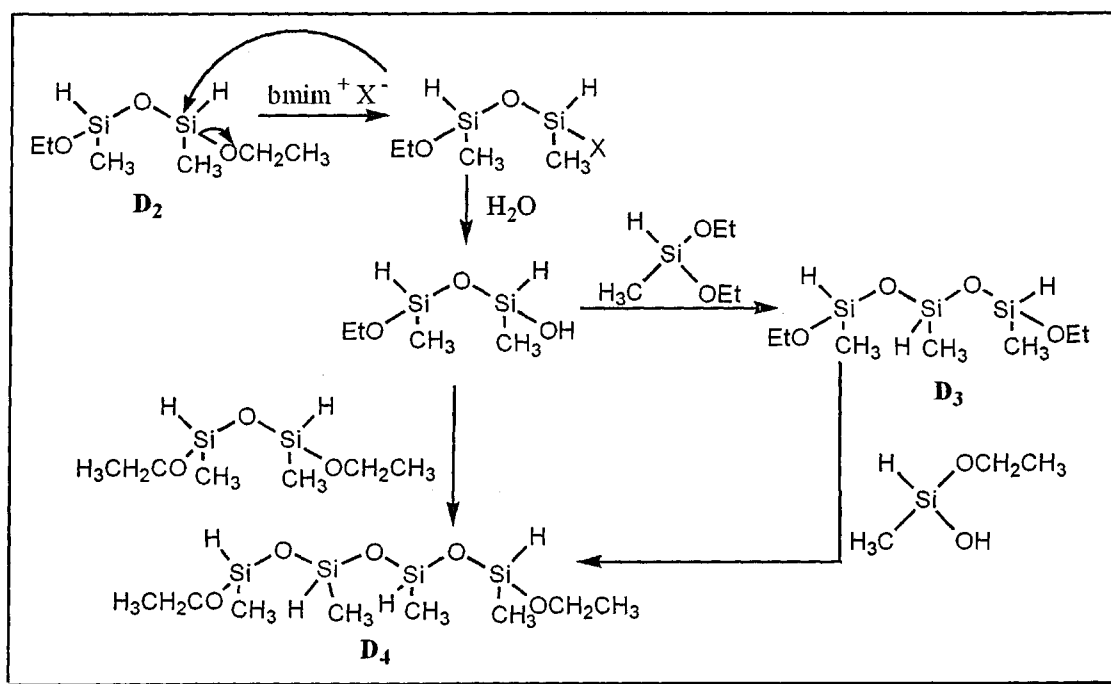
and the two central silicon atoms at  $-25.83$  ppm and  $-34.95$  ppm respectively. We followed the reaction using  $^{29}\text{Si}$  NMR spectroscopy and we could see the formation of the  $\text{D}_2$  after one day, then  $\text{D}_3$  and  $\text{D}_4$  after 3 days. The mechanism of the formation of  $\text{D}_2$  is shown in Scheme 57:



**Scheme 57: Formation of  $\text{D}_2$  silicon species in ionic liquids**

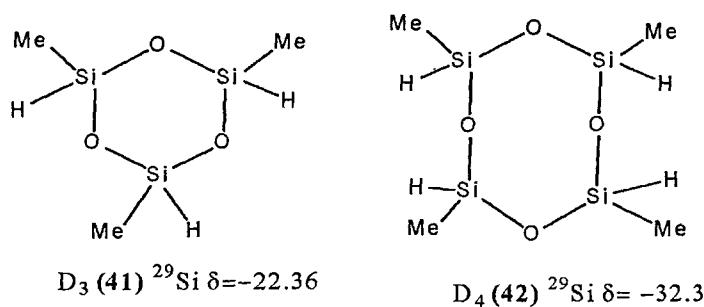
The anion of the ionic liquid attacks the silicon atom accompanied by the loss of one ethoxy group. The water, present in the ionic liquid, then attacks the silicon atom and ejects the leaving  $\text{X}^-$ . The OH of the resulting alkoxy-silanol attacks another silicon atom to give the siloxane  $\text{D}_2$ . The proposed mechanism for the formation of  $\text{D}_3$  and  $\text{D}_4$  starts with the formation of  $\text{D}_2$ , which then gives  $\text{D}_3$  and  $\text{D}_4$  as shown in Scheme 58.





**Scheme 58: Mechanism of formation of  $D_3$  and  $D_4$  by expansion of  $D_2$**

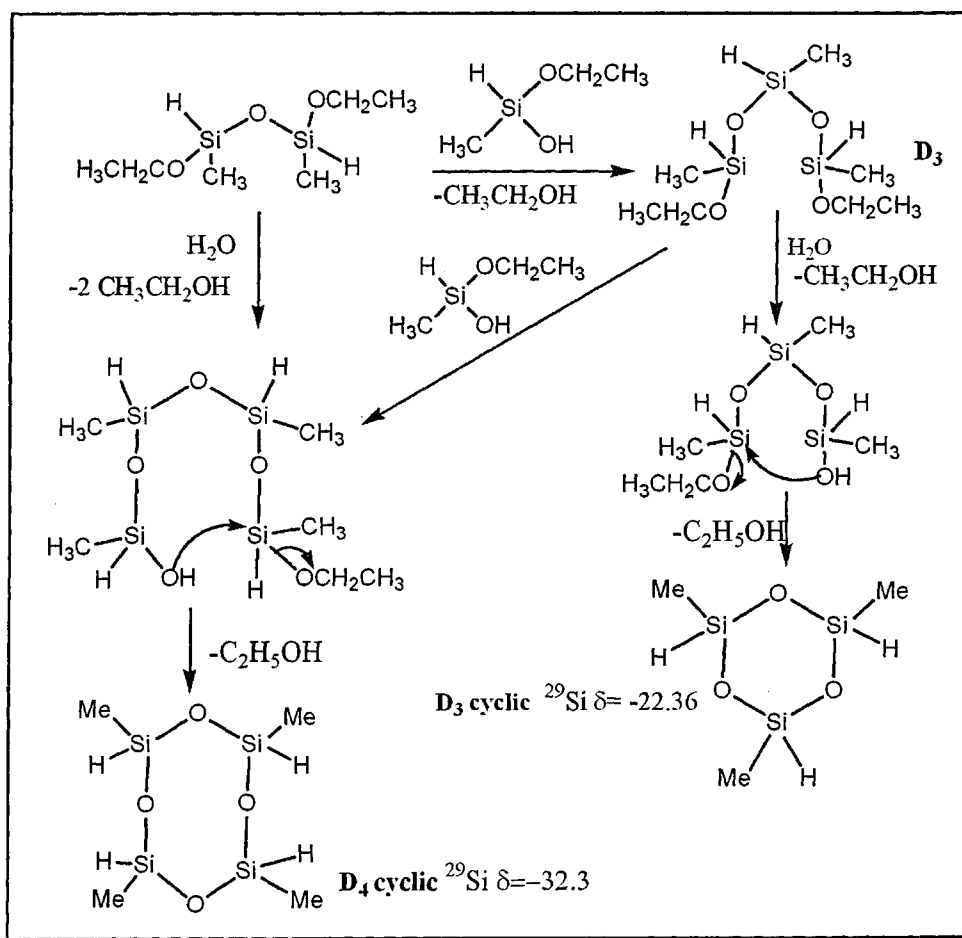
We tried to prepare longer chain siloxanes, and subsequently studied the reaction of alkoxy silanes with ionic liquids in an ultrasound bath for three days. The  $^{29}Si$  NMR spectrum showed the formation of linear  $D_2$ ,  $D_3$  and  $D_4$  siloxanes but in this case cyclic species were also seen, as shown in Figure 14:



**Figure 14: Cyclic  $D_3$  and  $D_4$  siloxane.**

The cyclic species formed are  $D_3$ : three silicon atoms attached to each other via oxygen bonds to form a six-membered ring, and  $D_4$ : four silicon atoms attached via oxygen bonds to give an eight membered-ring. In both cases the silicon

atoms in each ring have the same environment and show a single peak in the  $^{29}\text{Si}$  NMR spectra signal at  $-22.36$  ppm for  $\text{D}_3$  and  $-32.3$  for  $\text{D}_4$ . The use of ultrasound leads to localised heating that might promote the formation of cyclic compounds. The mechanism of the formation of such species is shown in Scheme 59.



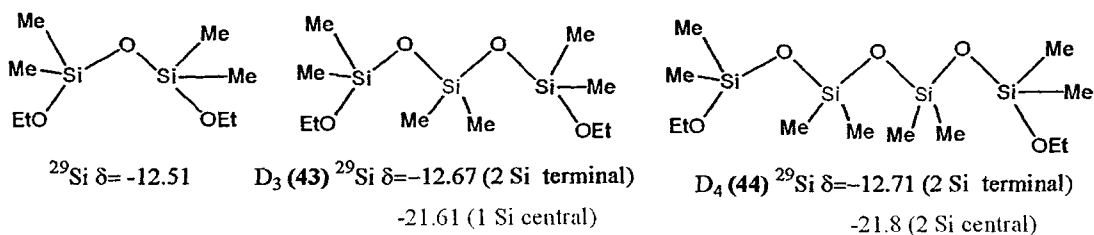
Scheme 59: Formation of cyclic  $\text{D}_3$  and  $\text{D}_4$  via linear  $\text{D}_3$  and  $\text{D}_4$  respectively.

The mechanism involves the formation of linear siloxanes which then rearrange into cyclic siloxanes. The reaction ends up as a mixture of linear and cyclic siloxanes and it is not possible to get the cyclic disiloxane species in the absence of linear species.

We followed this reaction with time and saw the formation of D<sub>2</sub> siloxane after one day. We then observed the formation of both D<sub>3</sub> and D<sub>4</sub> linear and cyclic siloxanes so the rearrangement of the linear species to give the cyclics must be a fast reaction which occurs in the presence of ultrasound but not following conventional conditions such as heating at 60°C. No Q silicon signals were observed, so there was no loss of H in this reaction.

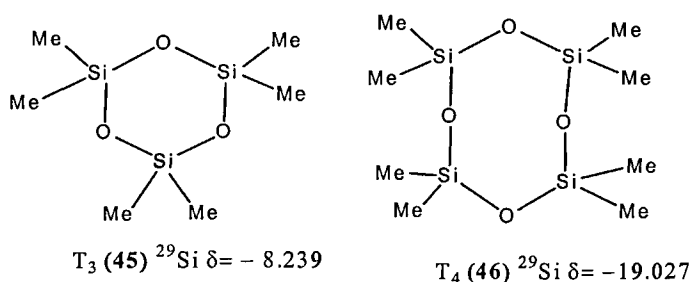
#### 4.3.2-Hydrolysis/condensation reactions of Me<sub>2</sub>Si(OEt)<sub>2</sub> in ionic liquids.

Me<sub>2</sub>Si(OEt)<sub>2</sub> was stirred at 60 °C in [bmim][OTf] and [bmim][NTf<sub>2</sub>] for three days and gave the linear disiloxanes: D<sub>2</sub>, D<sub>3</sub>, D<sub>4</sub> as illustrate in Figure 15. The individual species were not isolated, since it was difficult to separate them using column chromatography.



**Figure 15: Linear D<sub>2</sub>, D<sub>3</sub>, D<sub>4</sub> siloxanes obtained by reacting Me<sub>2</sub>Si(OEt)<sub>2</sub> with ionic liquids**

The reaction was carried out using ultrasound and resulted in a range of signals in the <sup>29</sup>Si NMR in the region of -8 to -22 ppm, corresponding to linear and cyclic siloxanes. For the cyclic siloxanes we obtained two signals at -8.2 and -19.03 ppm in a ratio of 3:4 corresponding to D<sub>3</sub> and D<sub>4</sub> respectively, as shown in Figure 16



**Figure 16: Cyclic  $T_3$ ,  $T_4$  siloxanes obtained by reacting  $\text{Me}_2\text{Si}(\text{OEt})_2$  with ionic liquids under the influence of ultrasound**

4.3.3-Hydrolysis/condensation reactions of  $\text{RSi}(\text{OEt})_3$ , where R = methyl, hexyl, phenyl and benzyl, in ionic liquids.

$\text{MeSi}(\text{OEt})_3$ ,  $(\text{EtO})_3\text{Si}[(\text{CH}_2)_5\text{Me}]$ ,  $(\text{EtO})_3\text{SiC}_6\text{H}_5$ ,  $(\text{EtO})_3\text{SiCH}_2\text{C}_6\text{H}_5$  were reacted in ionic liquids in order to obtain the corresponding T siloxanes. These species contain silicon atoms adjacent to three oxygen atoms. We now expected to see peaks in the  $^{29}\text{Si}$  NMR spectroscopy in the region  $-50$  to  $-65$  ppm. The reaction was carried out with stirring at  $60^\circ\text{C}$  and showed the formation of  $T_2$ ,  $T_3$  and  $T_4$  linear siloxanes. The data are reported in Table 50:

Silanes	$\delta\text{Si}$ ppm	Products	reference
	-50.61	$[\text{MeSi}(\text{OEt})_2]_2\text{O}$	172
$\text{MeSi}(\text{OEt})_3$	-53.5; -62.8	$T_3$ (47)	173
	-53.65; -70.02	$T_4$ (48)	174
	-52.5	$[\text{C}_6\text{H}_{13}\text{Si}(\text{OEt})_2]_2\text{O}$	
$(\text{EtO})_3\text{SiC}_6\text{H}_{13}$	-53.5; -62.8	$T_3$ (49)	175
	-53.65; -70.02	$T_4$ (50)	
	-65.85	$[\text{C}_6\text{H}_5\text{Si}(\text{OEt})_2]_2\text{O}$	176
$(\text{EtO})_3\text{SiC}_6\text{H}_5$	-66.18; -74.9	$T_3$ (51)	177
	-66.36; -75.11	$T_4$ (52)	
	-59.41	$[\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{OEt})_2]_2\text{O}$	
$(\text{EtO})_3\text{SiCH}_2\text{C}_6\text{H}_5$	-59.57; -70.1	$T_3$ (53)	178
	-59.81; -70.29	$T_4$ (54)	

**Table 50:  $^{29}\text{Si}$  NMR chemical shifts of siloxanes obtained from triethoxysilanes.**

In general signals corresponding to the terminal silicon atoms had a chemical shift smaller than the central silicon atoms. This is due to the difference in environment: the terminal silicon atoms are surrounded by two oxygen atoms from the alkoxy groups (OEt) and one oxygen atom from the Si-O-Si bridge, whereas the central silicon is surrounded by two oxygen atoms from the Si-O-Si bridge and one oxygen atom from the alkoxy group (OEt).

#### 4.3.4- Hydrolysis/condensation reaction of $\text{CH}_3\text{C}_6\text{H}_4\text{Si}(\text{OMe})_3$ and *cyclopentyl* $\text{Si}(\text{OMe})_3$ in ionic liquids.

$\text{CH}_3\text{C}_6\text{H}_4\text{Si}(\text{OMe})_3$  and *cyclopentyl* $\text{Si}(\text{OMe})_3$  were also reacted in ionic liquids. The reaction with  $\text{CH}_3\text{C}_6\text{H}_4\text{Si}(\text{OMe})_3$  gave linear  $\text{T}_2$ ,  $\text{T}_3$  and  $\text{T}_4$  siloxanes in the region of  $-62$  to  $-73$  ppm. This is as expected for a silicon adjacent to an  $\text{sp}^2$  carbon.

The reaction mixture from *cyclopentyl* $\text{Si}(\text{OMe})_3$  was analysed by  $^{29}\text{Si}$  NMR spectroscopy and showed signals in the region  $-51$  to  $-62$  ppm. Both data are shown in Table 51.

Silanes	$\delta\text{Si}$ ppm	Products	references
	-62.5	$[\text{CH}_3\text{C}_6\text{H}_4\text{Si}(\text{OEt})_2]_2\text{O}$	
$(\text{MeO})_3\text{SiC}_6\text{H}_4\text{CH}_3$	-62.83; -72.7	$\text{T}_3$ (55)	
	-63; -72.93	$\text{T}_4$ (56)	
	-51.76	$[\text{c-pentylSi}(\text{OMe})_2]_2\text{O}$	173
<i>c</i> -pentyl $\text{Si}(\text{OMe})_3$	-52.1; -61.5	$\text{T}_3$ (57)	
	-52.34; -61.74	$\text{T}_4$ (58)	

**Table 51:**  $^{29}\text{Si}$  NMR chemical shifts of siloxanes using dimethoxysilanes.

### 4.3.5-Summary of the hydrolysis/condensation reactions of silanes with ionic liquids.

The two ionic liquids, [bmim][OTf] and [bmim][NTf<sub>2</sub>], are able to attack the silicon atom of a silane and catalyse the formation of siloxanes. Starting with a dialkoxysilane the reaction gave the D<sub>2</sub>, D<sub>3</sub> and D<sub>4</sub> cyclic or linear siloxanes. With trialkoxysilanes the reaction affords T<sub>2</sub>, T<sub>3</sub> and T<sub>4</sub> linear siloxanes. It is interesting to note that in all cases only X<sub>2</sub>, X<sub>3</sub> and X<sub>4</sub> species were formed and not longer siloxane chains. This is may be due to the fact that the reaction runs out of water in the ionic liquids. The siloxane species formed are linear if the reaction is stirred at 60 °C; however, both cyclic and linear species are obtained if the reaction is carried out using ultrasound. The nature of the alkoxysilane and the nature of the substituents on the silicon atom affect the <sup>29</sup>Si NMR chemical shift. Table 52 summarises the different species and silicon shifts obtained in the reaction.

Silanes	δ Si ppm	Products	references
MeHSi(OEt) <sub>2</sub>	-25.56	[MeHSiOEt] <sub>2</sub> O	164
	-25.47; -34.65	D <sub>3</sub> ( <b>39</b> )	166
	-25.83; -34.95	D <sub>4</sub> ( <b>40</b> )	166
	-12.51	[Me <sub>2</sub> SiOEt] <sub>2</sub> O	167, 168
Me <sub>2</sub> Si(OEt) <sub>2</sub>	-12.67; -21.61	D <sub>3</sub> ( <b>43</b> )	169
	-12.71; -21.8	D <sub>4</sub> ( <b>44</b> )	

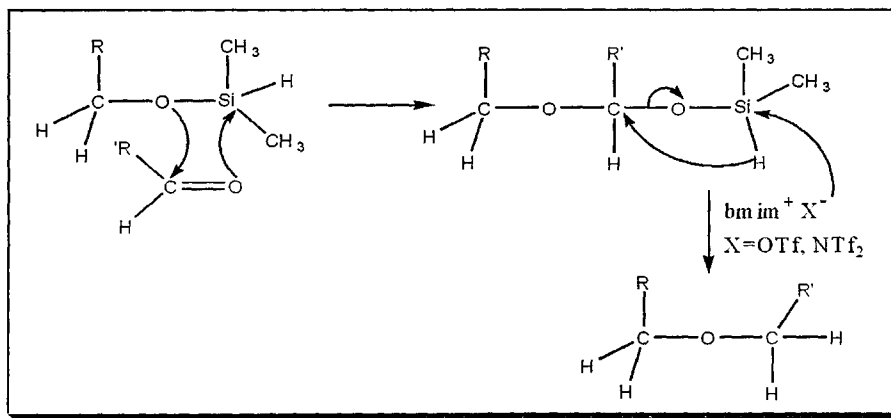
**Table 52:** <sup>29</sup>Si NMR chemical shifts of siloxanes using diethoxysilanes.

#### 4.4- Reactions of alkoxydialkylsilanes with aldehydes in the presence of ionic liquids.

We earlier studied the reaction of alkoxydialkylsilanes with aldehydes in the presence of salts, which resulted in the exclusive formation of mixed ethers. In this section we examine the reduction of aldehydes using alkoxydialkylsilanes as reducing agents and ionic liquids as the promoter of the reaction. We still expect the formation of the mixed ether but a change in the solvent could affect the yield of products obtained.

##### 4.4.1- Reduction of benzaldehyde with $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$ in ionic liquids.

Benzaldehyde was reacted with  $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$  in the ionic liquids [bmim][OTf] and [bmim][NTf<sub>2</sub>] and the products were analysed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. <sup>1</sup>H NMR spectroscopy showed a singlet at 4.47 ppm corresponding to the OCH<sub>2</sub>Ph group and a triplet at 3.66 ppm corresponding to the OCH<sub>2</sub>R of the benzyl octyl ether. <sup>13</sup>C NMR spectroscopy confirmed the formation of the mixed ether, showing two signals in the 70 ppm region corresponding to a carbon next to an oxygen. The isolated yield of benzyloctyl ether is 88 % and 87 % in [bmim][OTf] and [bmim][NTf<sub>2</sub>], respectively. The reduction of benzaldehyde with alkoxydialkylsilanes is straightforward in ionic liquids since the reaction involves a two phase system that allows the easy separation of the reagents and products. The mechanism is similar to that proposed using salts as nucleophiles and is shown in Scheme 60:



**Scheme 60: Mechanism of formation of a mixed dialkyl ether in ionic liquids.**

#### 4.4.2-Reduction of benzaldehyde with $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$ in ionic liquids

Benzaldehyde was also reduced by  $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$  in ionic liquids to give the mixed benzyl butyl ether in 92-96 % yield depending on the nature of the ionic liquid. If we compare this yield with that obtained in the formation of benzyl octyl ether we see that the butoxydimethylsilane is possibly more effective in the reduction of benzaldehyde than the octyloxydimethylsilane. We can also compare this with the yield obtained using salts (85 %), which shows that the reaction using an ionic liquid gave a slightly better yield, probably due to the easier separation of the products from the ionic liquids as there is no loss due to washing the mixture as was necessary in the presence of salts.

#### 4.4.3-Reduction of butanal with $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$ or octanal with $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$ in ionic liquids.

Butanal was reacted with  $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$  in ionic liquids in order to form the butyl octyl ether. The reduction was also performed by reacting octanal with  $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$ , which also gave the butyl octyl ether. The respective



yields obtained for these two reactions are 75 % and 86 % respectively. These yields confirm that butoxysilane is a more effective reducing agent than octyloxysilane. The steric effect of the octanal compare to the butanal is negligible compared to the reactivity of the alkoxysilanes. The  $^1\text{H}$  NMR spectra showed signals at 3.35 ppm and 3.41 ppm and the  $^{13}\text{C}$  NMR spectra showed two signals at 70.2 and 72.8 ppm, which corroborate the presence of the two  $\text{OCH}_2$  groups in the product.

#### 4.4.4-Summary and conclusions.

Alkoxydialkylsilanes are good reducing agents for the reduction of aldehydes in ionic liquids, to give exclusively the mixed ether. This therefore provides an alternative to Williamson's syntheses. The yield of mixed ethers obtained depends on the nature of the aldehydes and the alkoxydialkylsilanes. Bulky alkyl- and alkoxy groups reduced the yield of the mixed ether obtained. We observed a better yield of mixed ether in the reaction using the ionic liquid than the reaction using the salts as promoters. This improvement is due to a better separation of products from reagents in the ionic liquid. The yields are summarised in Table 53.

<b>RCHO R =</b>	<b><math>\text{C}_6\text{H}_5</math></b>	<b><math>\text{C}_6\text{H}_5</math></b>	<b><math>(\text{CH}_2)_6\text{CH}_3</math></b>	<b><math>(\text{CH}_2)_2\text{CH}_3</math></b>
<b>R'OSiHMe<sub>2</sub>R' =</b>	<b><math>(\text{CH}_2)_7\text{CH}_3</math></b>	<b><math>(\text{CH}_2)_3\text{CH}_3</math></b>	<b><math>(\text{CH}_2)_3\text{CH}_3</math></b>	<b><math>(\text{CH}_2)_7\text{CH}_3</math></b>
[bmim][OTf]	88%	96%	86%	80%
[bmim][NTf <sub>2</sub> ]	87%	92%	81%	75%

**Table 53: Isolated yield of mixed ethers obtained reacting aldehyde and alkoxyhydrosilane in ionic liquids.**

## 4.5-Hydrosilylation of alkenes in ionic liquids

In this section we report the hydrosilylation of alkenes with simple silanes (triethoxysilane and triethylsilane) in ionic liquids. A large amount of work on the hydrosilylation of alkenes has been reported in the literature and shows that the ratio of  $\alpha$ - to  $\beta$ - addition of the silane depends upon different factors, as described in the introduction. We have examined the influence of the solvent by comparing a normal solvent, such as THF, and ionic liquid solvents in the hydrosilylation of a range of alkene compounds. The different products expected for the  $\alpha$ - and  $\beta$ - additions are shown in Figure 23.  $\beta$ - Products are coloured in red and  $\alpha$ - products are in blue.

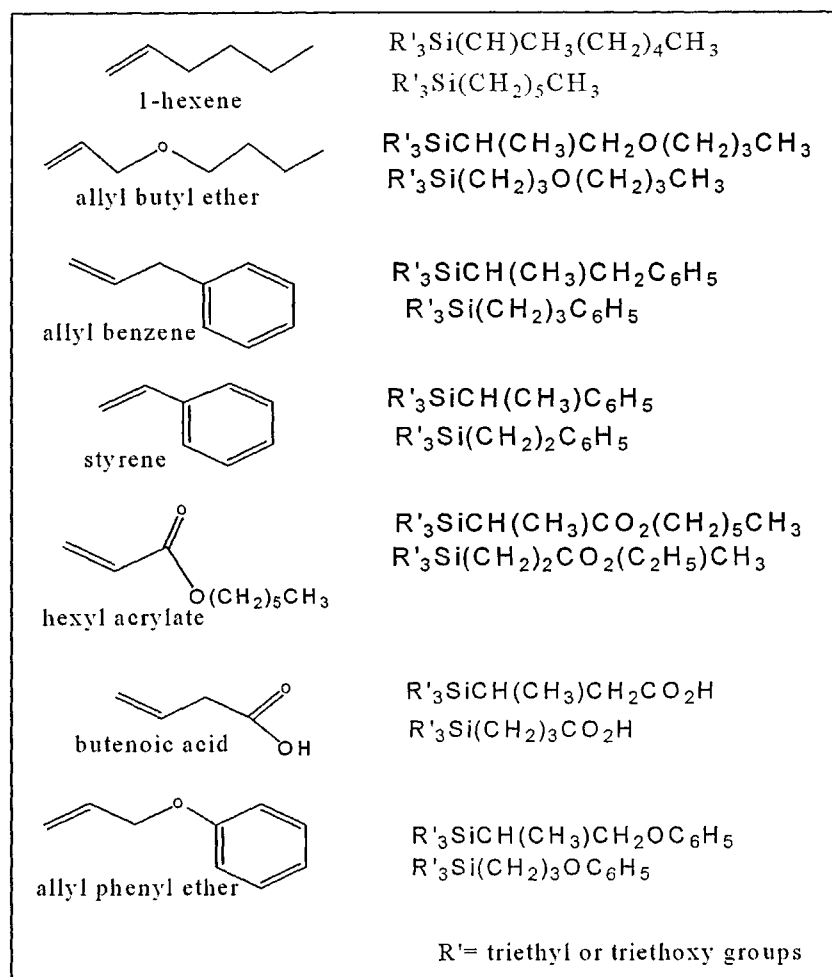


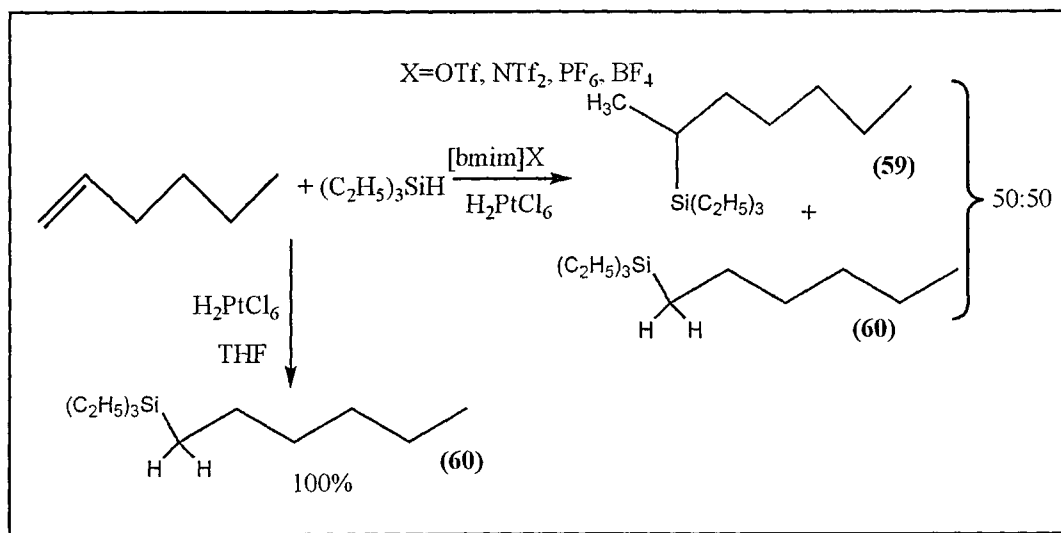
Figure 23: Alkenes used and their hydrosilylation products

A 0.2 mole l<sup>-1</sup> solution of Speier's catalyst and a 3 % solution of Karstedts catalyst in toluene (provided by Dow Corning) were used to promote the hydrosilylation reactions.

#### 4.5.1-Hydrosilylation of alkenes with triethylsilane in ionic liquids using Speier's catalyst

##### 4.5.1.1-Hydrosilylation of hex-1-ene

Hex-1-ene was reacted with triethylsilane in ionic liquids in the presence of a 0.2 mole l<sup>-1</sup> solution of chloroplatinic acid in isopropanol to give two major products corresponding to the  $\alpha$ - and  $\beta$ - addition products with a ratio of 50:50 in 33 % isolated yield. The <sup>1</sup>H NMR spectrum contained two key signals: one from the CH<sub>3</sub> of the  $\beta$ - product which appears as a doublet at 1.41 ppm and the other from the CH<sub>2</sub> of the  $\alpha$ - product which appears as a triplet at 0.49 ppm, confirming the formation of the two adducts. The integration of the two signals led to estimation of the  $\alpha$  :  $\beta$  ratio. There was little difference in reaction yields, time of reaction or  $\alpha$  :  $\beta$  ratio when different ionic liquids were employed. The corresponding reaction in THF give only the  $\beta$  product, as shown in Scheme 61.

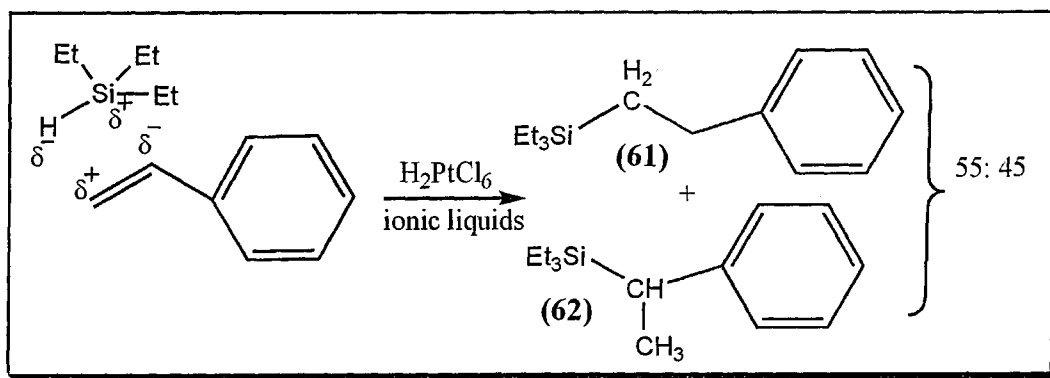


**Scheme 61: Hydrosilylation of hex-1-ene.**

Clearly the nature of the solvent (THF or ionic liquid) does affect the ratio of  $\alpha$  :  $\beta$  adducts obtained. This could be due to the solubility of the different reagents and products and also to the use of a very polar solvent such as an ionic liquid.

#### 4.5.1.2-Hydrosilylation of styrene

Styrene underwent hydrosilylation with triethylsilane in an ionic liquid and gave a mixture of the two  $\alpha$ - and  $\beta$ - products. The  $\alpha$  :  $\beta$  ratio was 55:45. This shows a slight change in favour of the  $\alpha$ - product, compared to hex-1-ene, which may be due to the conjugation with the phenyl group, described in Scheme 62. The isolated yield of the mixture of the two products is 29 %. The  $^{29}\text{Si}$  NMR spectroscopy showed two distinctive signals corresponding to the two different silicon atoms. The silicon atom in the  $\beta$ - product, with an environment of three ethyl groups and a  $(\text{CH}_2)_2\text{Ph}$  group had a chemical shift of 6.89 ppm whereas the silicon atom in  $\alpha$ - product with three ethyl groups and a  $\text{CH}(\text{CH}_3)\text{Ph}$  group had a chemical shift of 6.71 ppm.



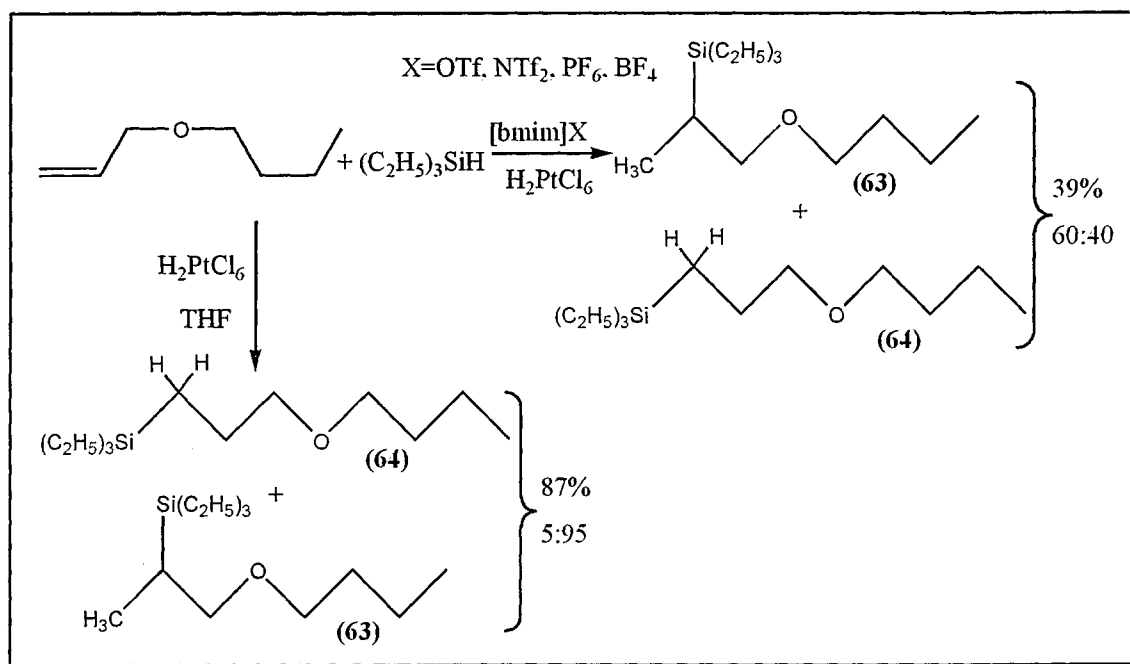
**Scheme 62: Hydrosilylation of styrene**

The influence of phenyl group on promoting  $\alpha$ - addition is also observed when THF was used as the solvent since the reaction gave an  $\alpha$ :  $\beta$  ratio of 5:95 instead of the 100 %  $\beta$ - addition seen for the hydrosilylation of hex-1-ene. These results suggest that the use of ionic liquid as solvents promotes the formation of the  $\alpha$ - addition product.

#### 4.5.1.3-Hydrosilylation of allyl butyl ether

Allyl butyl ether reacted with triethylsilane in ionic liquids in the presence of chloroplatinic acid to give both the  $\alpha$ - and  $\beta$ - products in an  $\alpha$  :  $\beta$  ratio of 60:40 and in 39 % yield, as shown in Scheme 63. The  $^1\text{H}$  NMR spectrum showed two key signals for the calculation of the  $\alpha$  :  $\beta$  ratio: the  $\text{CH}_3$  of the  $\alpha$ - product, which is a doublet at 0.72 ppm, and the  $\text{SiCH}_2$  of the  $\beta$ - product, which is a triplet at 0.08ppm. The  $^{29}\text{Si}$  NMR spectrum also confirmed the formation of these two products of hydrosilylation since we observed two signals at 8.79 and 7.13 ppm. If we compare these results for the allyl butyl ether with those for hex-1-ene, we see that the  $\alpha$ - product is more predominant in the hydrosilylation reaction of the allyl butyl ether than with the hex-1-ene. The Chalk Harrod mechanism suggests the outcome is influenced by the solvent used and the nature of the substituent

of the alkene, which includes electronic factors. The reaction was carried out under reflux at 50 °C for three days, and leaving the reaction longer did not change the  $\alpha$  :  $\beta$  ratio. Changing the solvent clearly affected the ratio of the  $\alpha$ - and  $\beta$ - product; in THF the reaction gave a  $\alpha$  :  $\beta$  ratio of 5:95 which show that the  $\beta$ - product is the main product. In this case, the electronic effect of the oxygen of the allyl group allowed the formation of 5 %  $\alpha$ - addition product which was not obtained in the hydrosilylation of hex-1-ene. This suggests that the electronic effect of the alkene substituent is more significant in very polar solvents such as ionic liquids.



**Scheme 63: Hydrosilylation of allyl butyl ether**

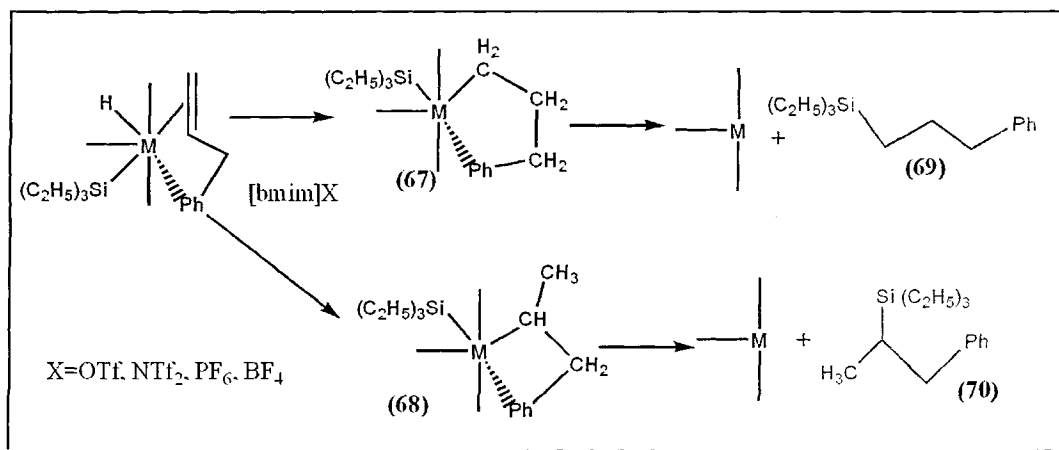
#### 4.5.1.4-Hydrosilylation of allyl phenyl ether

Hydrosilylation of allyl phenyl ether with triethylsilane in the presence of chloroplatinic acid gave both hydrosilylated  $\alpha$ - and  $\beta$ - addition products in an  $\alpha$  :  $\beta$  ratio of 40:60. The hydrosilylation of allyl phenyl ether leads to less of the

branched  $\alpha$ - product than the hydrosilylation of the allyl butyl ether. This is may be due to a steric effect since the phenyl group is bulkier than the butyl group, so the less sterically hindered product is favoured.

#### 4.5.1.5-Hydrosilylation of allylbenzene.

The hydrosilylation of allylbenzene gave both  $\alpha$ - and  $\beta$ - compounds in a 30 % yield, with a preference for the  $\alpha$ - product, giving an  $\alpha$  :  $\beta$  ratio of 55: 45. The  $^{29}\text{Si}$  NMR spectrum shows two signals at 6.72 and 8.85 ppm corresponding to the  $\beta$ - and  $\alpha$ - products respectively. Although the phenyl group cannot conjugate with the double bond it still affects the polarisation leading to the formation of more  $\alpha$ - compound. An alternative explanation involves the formation of intermediates **(67)** and **(68)**, where the phenyl substituent co-ordinates with the platinum, as shown in Scheme 64. The difference in energy between the two intermediate is low and consequently either of these routes can occur.



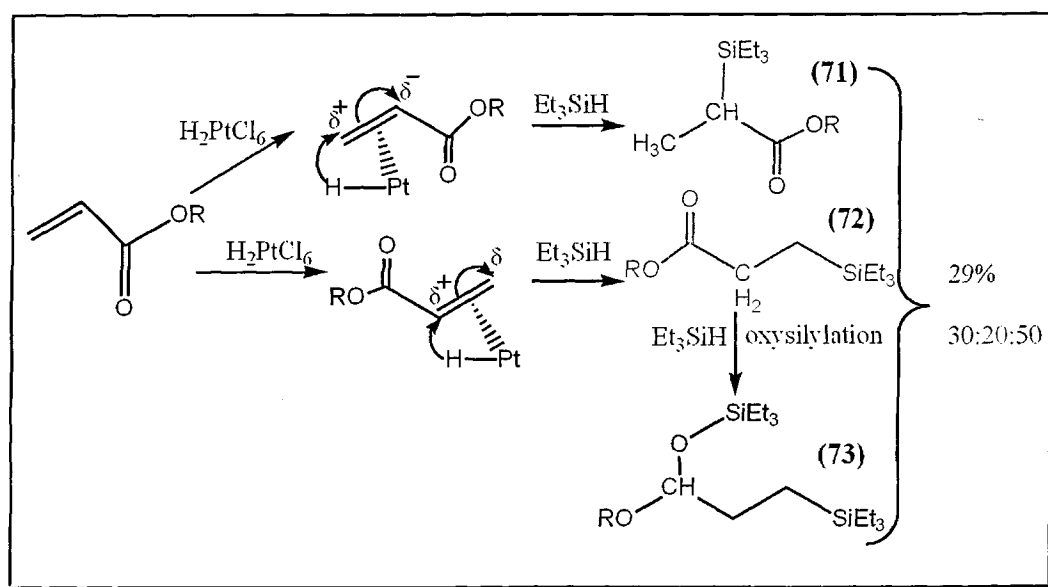
**Scheme 64:** Co-ordination of the phenyl group into the transition metal and formation of  $\alpha$ - and  $\beta$ - compounds.

The reaction was carried out in THF and gave only 5 % of the  $\alpha$ - product, as with the hydrosilylation of allyl butyl ether.

#### 4.5.1.6-Hydrosilylation of hexyl acrylate.

Hexyl acrylate was also treated with triethylsilane in ionic liquids in the presence of chloroplatinic acid. In this case a  $\text{CO}_2\text{R}$  group is the substituent on the alkene, which will enable conjugate addition effectively making the terminal carbon atom more electrophilic, thus favouring  $\alpha$ - addition.

The reduction gave a mixture of three products: the two expected products from hydrosilylation, and one corresponding to the formation of the  $\beta$ - hydrosilylation product followed by an oxysilylation of the carbonyl, as illustrated in Scheme 65.



Scheme 65: Hydrosilylation and oxysilylation of hexyl acrylate.

The  $^{29}\text{Si}$  NMR spectroscopy corroborates the presence of these three silicon species giving signals at 6.71, 8.14 and 16.13 ppm. The signal at 8.14 ppm corresponds to the silicon atom in the  $\alpha$ - product, the signal at 6.71 ppm arises from the silicon atom in the  $\beta$ - product (72), and the signal at 16.13 ppm arises from the silicon atom attached to the oxygen atom in (73).

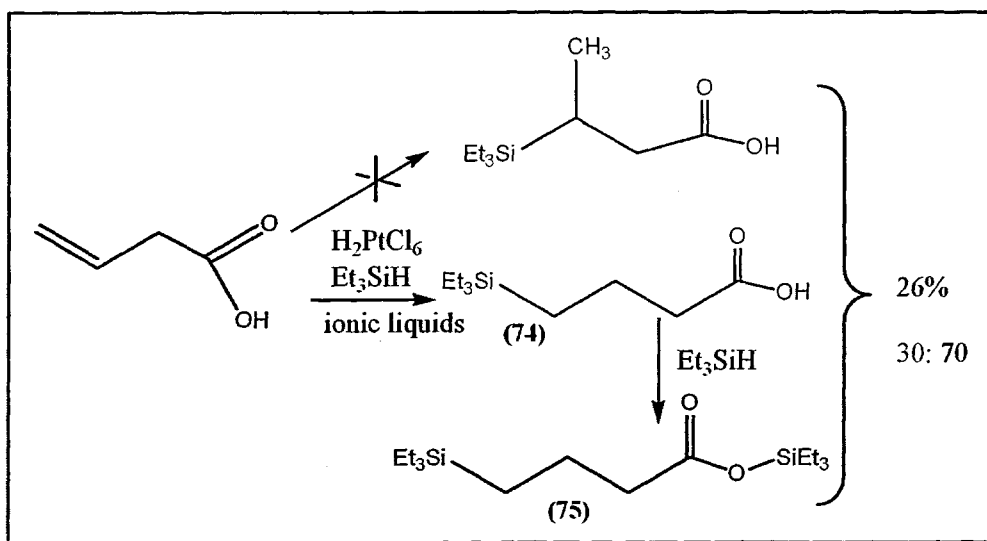


The  $^1\text{H}$  NMR spectrum integration enables us to obtain the  $\alpha : \beta$  ratio of the three different products. The mixture is obtained in 29 % yield and the ratio is 30:20:50 for the compounds (71): (72): (73) respectively.

In contrast to this result, the reaction in THF produced a mixture of 5 %  $\alpha$ -product and 95 % of  $\beta$ - product. No oxysilylation occurred during the hydrosilylation reaction. When the reaction was carried out in THF with a solution of chloroplatinic acid 10 $\times$  more concentrated no change in the reaction ratio and yield was observed. This suggests the reaction is affected only by the use of the ionic liquid.

#### 4.5.1.7-Hydrosilylation of but-3-enoic acid.

Hydrosilylation of but-3-enoic acid with triethylsilane produced only the  $\beta$ -product and the product of reaction of the OH of the acid group in a ratio of 30:70 respectively. No silicon signal was observed which corresponded to an  $\alpha$ -hydrosilylation product. But-3-enoic acid does not involve conjugation of the alkene and carboxylic acid group and therefore the hydrosilylation is probably only controlled by steric factors producing solely the  $\beta$ - product. This  $\beta$ - product then reacts further reduced to give the final product with an extra signal at 25.05 ppm in the  $^{29}\text{Si}$  NMR spectroscopy.



Scheme 66

Similar results were observed in THF; that is, formation of the  $\beta$ -hydrosilylated product that undergoes further reduction of the OH of the acid group. The products (74) and (75) were formed in a 15: 85 ratio.

On comparing the hydrosilylations of the hexyl acrylate and the but-3-enoic acid we see that the carbonyl is reduced in the case of the ester but is not reduced in the carboxylic acid. In this latter case, the silicon exchanges with an OH.

#### 4.5.2-Hydrosilylation of alkenes with triethoxysilane in ionic liquids.

The hydrosilylation of alkenes in ionic liquids using triethoxysilane as the reducing agent in the presence of a  $0.2 \text{ mole l}^{-1}$  solution of chloroplatinic acid gave the results reported in Table 54. The hydrosilylations were also carried out in the organic solvent THF and the results are reported in the same Table. In order to compare these results with those obtained using triethylsilane as the reducing agent we have also summarised in the last two columns the results obtained in section 4.5.1.

Solvent Silane	Ionic liquids: bmimX (EtO) <sub>3</sub> SiH	THF (EtO) <sub>3</sub> SiH	bmimX Et <sub>3</sub> SiH	THF Et <sub>3</sub> SiH
Hex-1-ene	(EtO) <sub>3</sub> SiCH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> α:β= 52:48 40 % (76) and (77)	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> 100 % β	α:β=50:50 33 %	99 % β
Styrene	(EtO) <sub>3</sub> SiCH(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> α:β=55:45 29 % (78) and (79)	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> 90 % α : β = 40:60	α:β=60:40 23 %	74 % α : β=5:95
Allyl butyl ether	(EtO) <sub>3</sub> SiCH(CH <sub>3</sub> )CH <sub>2</sub> O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> (EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> α:β=50:50 48 % (80) and (81)	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> 95 % α : β=5:95	α:β=60:40 39 %	87 % α : β=5:95
Allyl phenyl ether	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> OC <sub>6</sub> H <sub>5</sub> α:β= 45:55 53 % (82) and (83)	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> OC <sub>6</sub> H <sub>5</sub> 92 % α : β= 45:55	α:β=40:60 42 %	89 % α : β= 45:55
Allyl benzene	(EtO) <sub>3</sub> SiCH(CH <sub>3</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> α:β= 65:35 38 % (84) and (85)	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> 93 % α : β = 5:95	α:β=55:45 30 %	85 % α : β=5:95
Hexyl acrylate	(EtO) <sub>3</sub> SiCH(CH <sub>3</sub> )CO <sub>2</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub> (EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub> CH[O(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub> ]O Si(OEt) <sub>3</sub> α:β:β oxy-silylation = 30:10:60 37 % (86), (87) and (88)	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub> 84 % α : β=5:95	α:β:β oxy-silylation = 30:20:50 29 %	74 % α : β=5:95
But-3- enoic acid	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H (EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> CO[OSi(OEt) <sub>3</sub> ] β:β oxy-silylation = 20:80 22 % (89) and (90)	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> CO[OSi(OEt) <sub>3</sub> ] 100 % β oxy-silylation	β:β oxy-silylation = 30:70 16 %	63 %

**Table 54: Results of the hydrosilylation of alkenes in ionic liquids and THF using triethyl- or triethoxysilane.**

As we observed in Section 4.5.1, the main products obtained are the two hydrosilylation products resulting from the α- and β- addition of triethoxysilane. If an ester or acid group is present in the alkenes then the initial product undergoes further reaction. Comparing the reactions using ionic liquid and THF, we see that the α: β ratio is different in the two solvents; ionic liquids promote the formation of the α- product. Apart from styrene and allyl phenyl ether, the others alkenes gave about 100 % of the β- product in THF. The presence of the phenyl group as a substituent on the alkenes encourages the formation of the α- product leading to a more 50:50 ratio.

The results obtained using triethoxysilane are rather similar to those obtained using triethylsilane, suggesting the nature of the silane does not greatly affect the α- to β- ratio of the products. The overall yields obtained are higher using

triethoxysilane compared to triethylsilane. Since hydrosilylation is faster with triethoxysilanes it is not surprising that we get a 70 % yield of OH reaction. The  $^{29}\text{Si}$  NMR spectrum shows distinctive sets of signals for the different hydrosilylated products, the first in the region of  $-42$  to  $-58$  ppm corresponding to a silicon atom surrounded by three oxygens, and around  $-81$  ppm corresponding to a silicon atom surrounded by four oxygens resulting from oxysilylation.

It is interesting to note that the yields of  $\alpha$ - and  $\beta$ - products obtained using  $\text{R}_3\text{SiH}$  and  $(\text{RO})_3\text{SiH}$  are in the range of 30-50 %. There is no trace of unreacted starting material in the  $^{29}\text{Si}$  NMR spectra, which suggest that these low yields may be due to the partial solubility of the  $\alpha$ - and  $\beta$ - products in the ionic liquids. A separation with a polar solvent such as ethyl acetate does not permit the extraction of the  $\alpha$ - and  $\beta$ - products leading to more moderate yield in the hydrosilylation reaction.

#### 4.5.3-Hydrosilylation of alkenes in the presence of Karstedt catalyst in ionic liquids.

The hydrosilylation of alkenes with triethoxysilane was carried out in ionic liquids in the presence of a 3 % solution of Karstedt catalyst in toluene (provided by Dow Corning). The reaction did not lead to any products of hydrosilylation after overnight reaction, and only the starting materials were recovered. The  $^1\text{H}$  NMR spectra confirmed the presence of three signals in the region of 5-6.5 ppm and the  $^{13}\text{C}$  NMR spectra showed two signals in the region of 110-150 ppm corresponding to the vinyl groups of the alkene. Leaving the

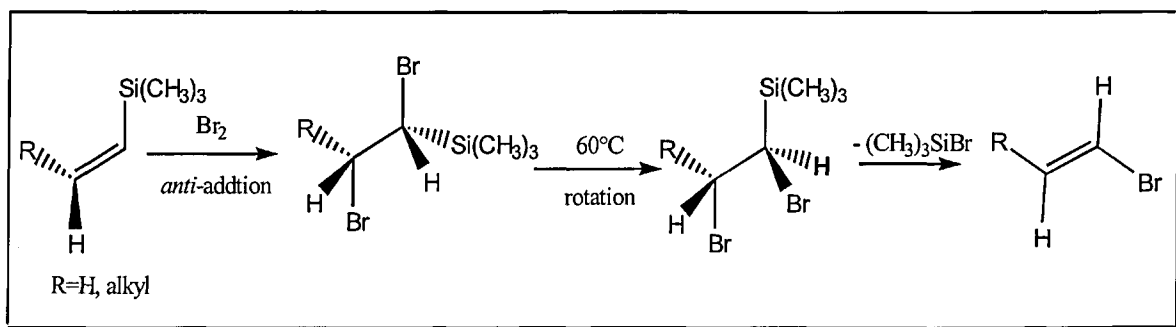
reaction longer (e.g. 3 days) did not show evidence for any hydrosilylation but showed the formation of trisiloxanes when the ionic liquids reacted with the silanes, as discussed in Section 4.3. The  $^{29}\text{Si}$  NMR spectra showed signals in the region of  $-50$  to  $-60$  ppm that are related to the formation of  $\text{T}_2$ ,  $\text{T}_3$  and  $\text{T}_4$  linear.

The lack of any evidence for hydrosilylation is almost certainly due to the non-solubility of the catalyst in the ionic liquids. Karstedt catalyst is provided as a solution in toluene which remained on the top of the ionic liquid as a separate organic phase. Good stirring had no effect on the reaction. When carried out in THF using Karstedt catalyst the reaction gave the expected hydrosilylation products<sup>179</sup>.

#### 4.6 Reactions of other nucleophiles in ionic liquids.

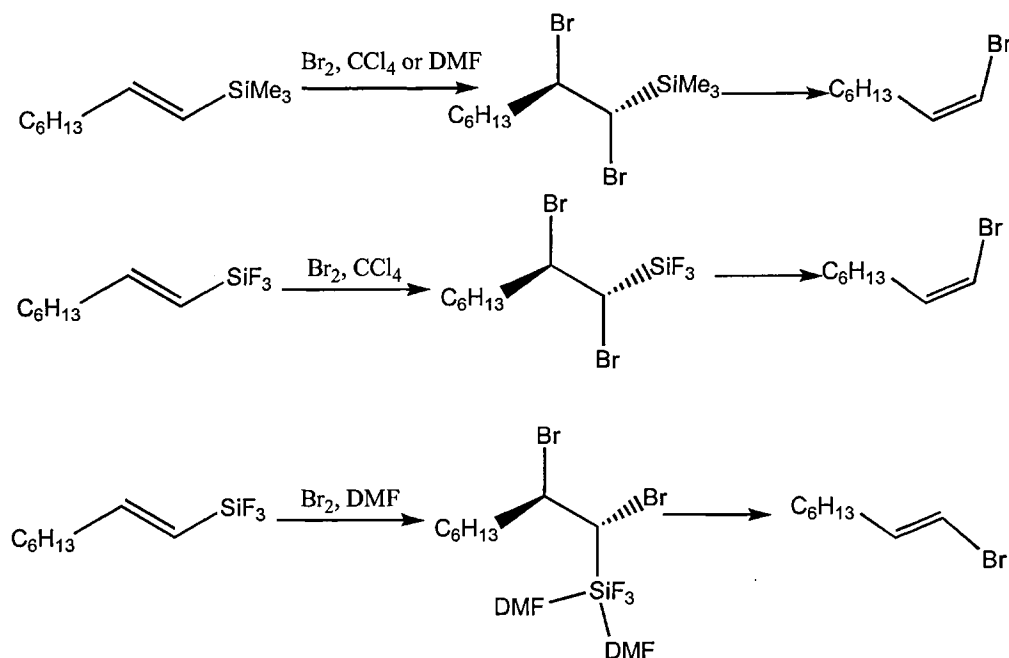
##### 4.6.1-Bromination of silanes.

Vinylsilanes react with halogens (e.g. bromine) to give both addition and substitution. These reactions proceed through *anti*-addition of the halogen, which may be followed by *anti*-elimination of  $\text{Me}_3\text{SiBr}$ , as described in Scheme 67<sup>178</sup>.



Scheme 67: Bromination of vinylsilane.

By contrast, the same reaction with a vinylsilane, which contains a silicon that can extend its co-ordination, gave the substitution product with retention of configuration. In the presence of a co-ordinating solvent the reaction also undergoes retention, but non co-ordinating solvents react with inversion of configuration, as shown in Figure 26<sup>179</sup>.



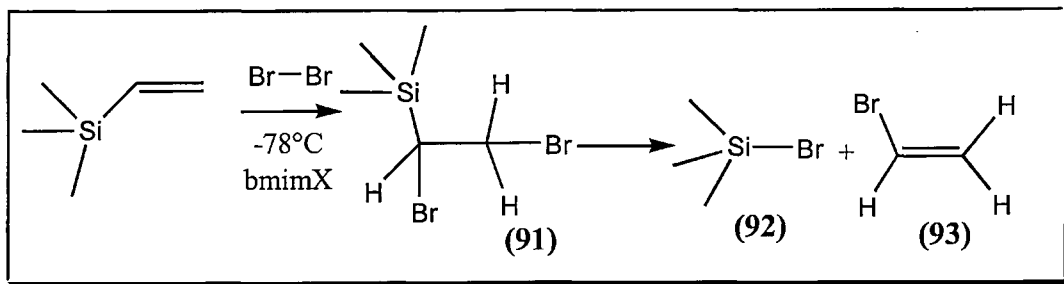
**Figure 26: Examples of inversion or retention of configuration observed during the bromination of vinylsilane.**

These examples show that the solvent affects the regioselectivity of the reaction<sup>180</sup>.

#### 4.6.1.1-Bromination of vinyltrimethylsilane.

In this case since the R group is a hydrogen there will be no evidence of stereoselectivity, but we can still examine whether the bromine is added to the vinyl silane and then undergoes rearrangement to give the vinyl bromide product. In the reaction mixture the <sup>29</sup>Si NMR spectra signal at -6.88 ppm corresponding to the silicon atom in the starting material disappeared

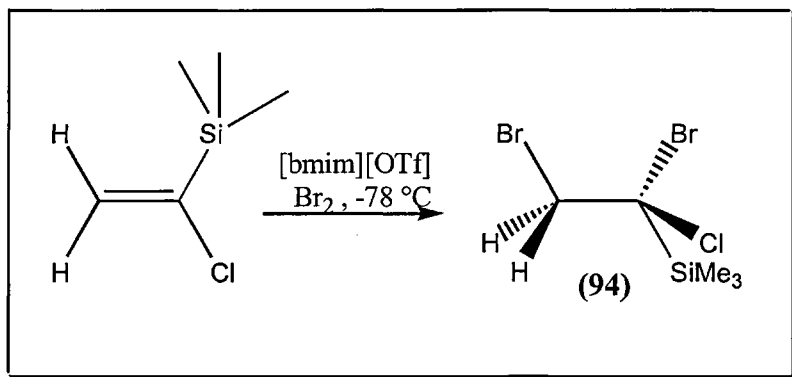
completely, and two signals at 6.02 and 27.43 ppm appeared confirming the formation of the products (91) and (92).



**Scheme 68: Bromination of vinyltrimethylsilane**

#### 4.6.1.2-Bromination of chlorovinyltrimethylsilane

1-Chlorovinyltrimethylsilane was reacted with bromine and produced (1-chloro-1,2-dibromoethyl)trimethylsilane by addition of bromine across the double bond. Elimination of bromotrimethylsilane did not occur in this case.

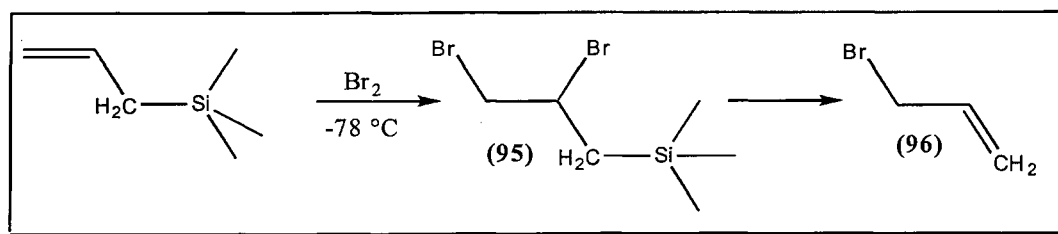


**Scheme 69: Bromination of chlorovinyltrimethylsilane**

#### 4.6.1.3-Bromination of allyltrimethylsilane

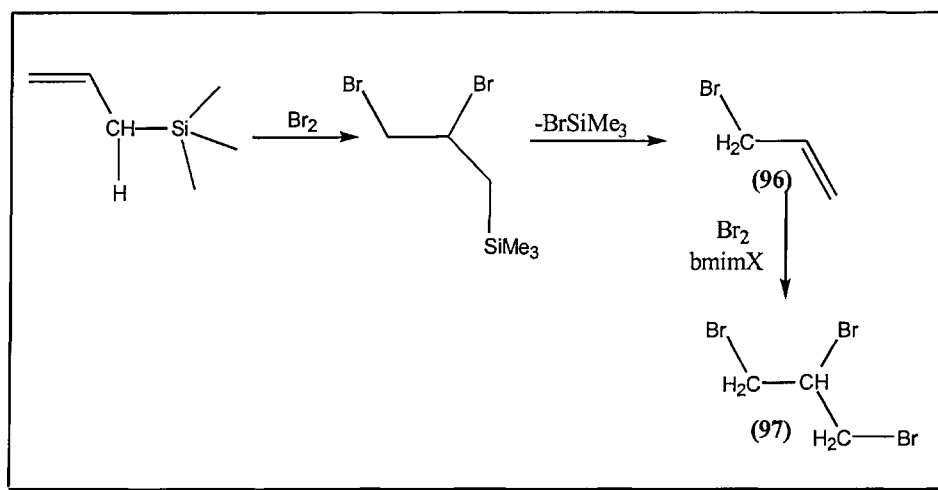
Allyltrimethylsilane reacts similarly to vinyltrimethylsilane with bromine in THF and gave the addition product (2,3-dibromopropyl)trimethylsilane, which subsequently rearranged to give the 3-bromopropene product.  $^1\text{H}$  NMR

spectrum shows evidence for the formation of these two products showing three signals in the region of 5-6 ppm corresponding to three hydrogen atoms on the vinyl group in (96) and three signals in the region of 3.45-3.9 corresponding to the three hydrogens atoms on the carbon-bromine groups in (95).



**Scheme 70: Bromination of allyltrimethylsilane**

In the presence of ionic liquids the reaction gave the 1,2,3-tribromopropane product (97). No  $^1\text{H}$  NMR signals were observed in the region of 5-6 ppm, suggesting the propene (96) undergoes further addition with  $\text{Br}_2$  in ionic liquid. The pathway is described in Scheme 71.

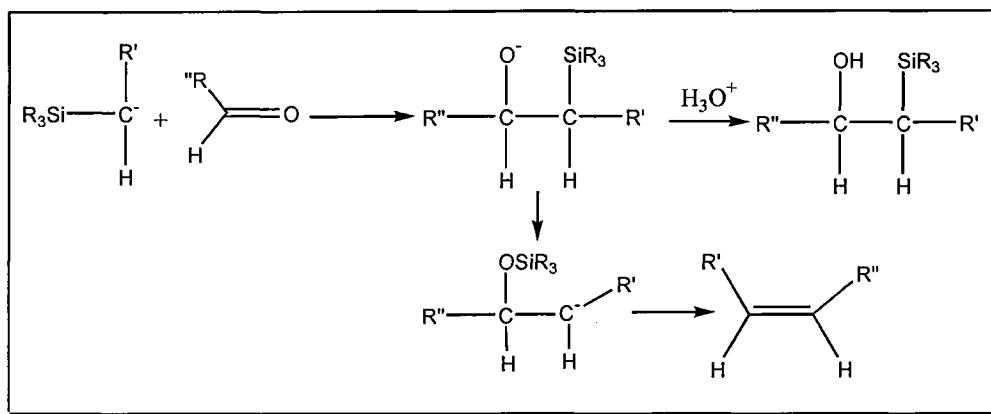


**Scheme 71: Bromination of allyltrimethylsilane in ionic liquids**



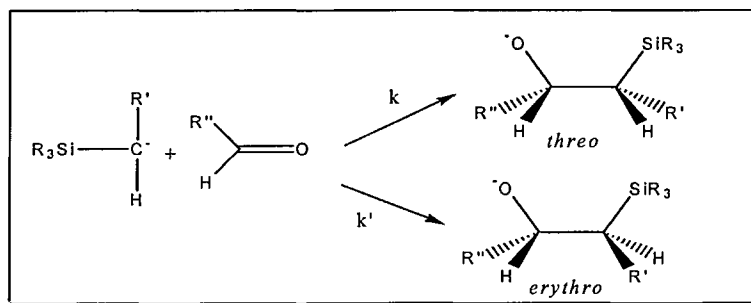
#### 4.6.2-The Peterson reaction.

$\alpha$ -Silyl carbanions react with aldehydes to give the corresponding  $\beta$ -silyl alkoxide which can then protonate to give the corresponding  $\beta$ -silyl alcohol or eliminate an alkoxy-silyl group to produce olefins, as described in Scheme 72. The formation of olefins using this route is known as the Peterson reaction<sup>181</sup>.



Scheme 72

The first step has been shown to be irreversible. Formation of the *cis* and *trans* alkenes has been reported in the literature using benzaldehyde as the carbonyl compound and the results suggest there is no back reaction once the  $\beta$ -silylalkoxide is formed<sup>182-185</sup>. In many cases, the *cis* and *trans* alkenes are produced in the same ratio. If formation of the  $\beta$ -silylalkoxide is rate limiting the stereochemical outcome depends upon the rate of formation of *threo* and *erythro*  $\beta$ -silylalkoxide, as shown in Scheme 73.



Scheme 73

In fact, the *cis* : *trans* ratio has been shown to depend on the nature of the substituent on the silicon atom. Bulky SiR<sub>3</sub> groups increase the formation of *Z* alkene since the steric effect of this bulky group slows down the approach of the carbanion to the aldehyde in the arrangement described in Figure 27.

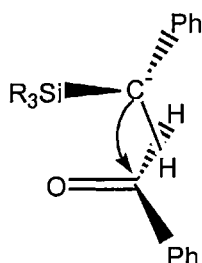


Figure 27

In this section we report one example of the Peterson reaction in ionic liquids. Benzaldehyde was reacted with benzyldis(trimethylsilane) in [bmim][OTf]. We expected that the ionic liquid would attack the silicon atom to give the  $\beta$ -silyl-carbanion, which would then react with the carbonyl group of the benzaldehyde.

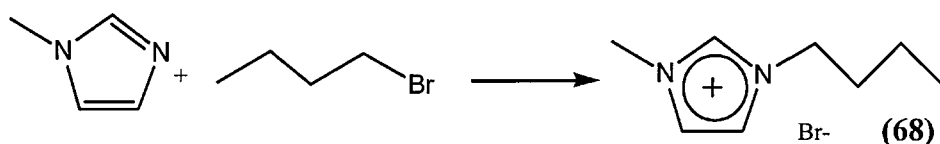
<sup>1</sup>H and <sup>13</sup>C NMR spectrum were used to analyse the reaction mixture, which showed one signal corresponding to the hydrogen on the carbonyl group of the benzaldehyde at 10 ppm, and one signal at 192.27 ppm corresponding to the carbon of the carbonyl. Also no change was observed in the <sup>29</sup>Si NMR spectra for the signal corresponding to the silicon atom in the benzyldis(trimethylsilane) at -6.9 ppm. Leaving the reaction longer or under reflux did not lead to any reaction. This suggests that the ionic liquid is not nucleophilic enough to cause the cleavage of the silicon-carbon bond, which allows the formation of the  $\beta$ -silyl carbanion.

# Chapter 5

## Chapter 5-Experimental for ionic liquid investigations

### 5.1-Preparation of ionic liquids:

#### 5.1.1-Preparation of $\text{bmim}^+\text{Br}^-$



1-Methylimidazole (166 ml, 2.08 mol) was placed in a two neck flask equipped with a condenser and a drying tube. Bromobutane (250 ml, 2.32mol) was added dropwise. The mixture was heated slowly with stirring to 50 °C using an oil bath. The appearance of a yellow liquid at the bottom of the flask confirmed that the reaction had occurred. After addition of bromobutane (over about 1 h), the mixture became more viscous and two phases were formed. The top one, which was light yellow, corresponded to the unreacted starting material, the bottom one which was dark yellow corresponded to the product. After the addition, the mixture was left with heating and stirring for about 20 min. The mixture was then cooled to room temperature.

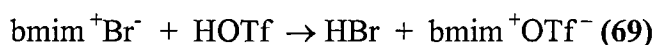
The mixture was dissolved in acetonitrile (150 ml or less), and stirred for 15 min at room temperature. The mixture was then shaken and the product precipitated out by the addition of the minimum amount of ethyl acetate (about 250 ml). Filtration under vacuum gave a pure sample of  $\text{bmim}^+\text{Br}^-$ .

If no solid appeared the mixture was placed in the fridge overnight. If there was no crystallisation after one night the side of the flask was scratched and some more ethyl acetate added, and replaced in the fridge for 1 h. The solvent was removed by filtration under vacuum and the solid was dried using a vacuum at 50 °C. The solid is air sensitive, so contact with air was avoided. Yield=291g, 64 %.

**bmim<sup>+</sup>Br<sup>-</sup> (68):**  $\delta_H$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.33 (CH<sub>3</sub>, t, <sup>3</sup>J = 7.5 Hz, 3H); 0.65 (CH<sub>2</sub>, m, 2H); 1.22 (CH<sub>2</sub>, m, 2H); 3.45 (NCH<sub>3</sub>, s, 3H); 3.74 (NCH<sub>2</sub>, t, <sup>3</sup>J = 7.3 Hz, 2H); 6.94 (NCH, d, <sup>3</sup>J = 3.5 Hz, 1H); 7.06 (NCH, d, <sup>3</sup>J = 3.5 Hz, 1H) and 9.57 (NCHN, s, 1H);  $\delta_C$  (75 MHz, d<sub>6</sub>-acetone, Me<sub>4</sub>Si) 13.06 (CH<sub>3</sub>); 19.02 (CH<sub>2</sub>); 31.76 (CH<sub>2</sub>); 36.31 (NCH<sub>3</sub>); 49.38 (NCH<sub>2</sub>); 121.91 (NCH); 123.47 (NCH) and 136.67 (NCHN) <sup>186</sup>.

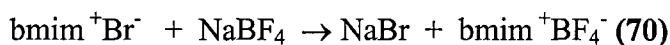
### 5.1.2-Preparation of other ionic liquids

bmim<sup>+</sup>Br<sup>-</sup> (50.12 g, 0.228 mol) was dissolved in water (150 ml) in a round bottom flask and placed in an ice bath. One equivalent of an appropriate acid or salt was added dropwise. After the addition (about 1 h), the mixture was extracted with cold dichloromethane (3×50 ml). The organic layer was washed with cold water (10 ml). The organic solvent was dried with magnesium sulfate and filtered. The solvent was removed using a rotary-evaporator. The ionic liquid was dried using a vacuum at 50 °C.



In this reaction one equivalent of trifluoromethanesulfonic acid (20.24 ml, 0.228 mol) was added dropwise with stirring. Yield=56 g, 81 %.

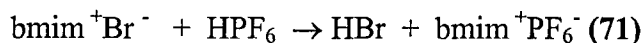
**bmim<sup>+</sup>OTf<sup>-</sup> (69):**  $\delta_H$  (300 MHz, d<sub>6</sub>-acetone, Me<sub>4</sub>Si) 3.12 (CH<sub>3</sub>, t, <sup>3</sup>J = 7.1 Hz, 3H); 3.52 (CH<sub>2</sub>, m, 2H); 4.09 (CH<sub>2</sub>, m, 2H); 6.31 (NCH<sub>3</sub>, s, 3H); 6.58 (NCH<sub>2</sub>, t, <sup>3</sup>J = 7.1 Hz, 2H); 9.87 (NCH, d, <sup>3</sup>J = 3.6 Hz, 1H); 9.95 (NCH, d, <sup>3</sup>J = 3.6 Hz, 1H) and 11.26 (NCHN, s, 1H);  $\delta_C$  (75 MHz, d<sub>6</sub>-acetone, Me<sub>4</sub>Si) 15.44 (CH<sub>3</sub>); 21.72 (CH<sub>2</sub>); 34.54 (CH<sub>2</sub>); 38.35 (NCH<sub>3</sub>); 51.91 (NCH<sub>2</sub>); 125.19 (NCH); 125.67 (CF<sub>3</sub>); 126.47 (NCH) and 139.47 (NCHN)<sup>83</sup>.



One equivalent of NaBF<sub>4</sub> (5.51 g, 0.232 mol) was added to the reaction mixture. Yield=40 g, 73 %

**bmim<sup>+</sup>BF<sub>4</sub><sup>-</sup> (70):**  $\delta_H$  (300 MHz, d<sub>6</sub>-acetone, Me<sub>4</sub>Si) 3.15 (CH<sub>3</sub>, t, <sup>3</sup>J = 7.1 Hz, 3H); 3.54 (CH<sub>2</sub>, m, 2H); 4.23 (CH<sub>2</sub>, m, 2H); 6.17 (NCH<sub>3</sub>, s, 3H); 6.48 (NCH<sub>2</sub>, t, <sup>3</sup>J = 7.15 Hz, 2H); 9.85 (NCH, d, <sup>3</sup>J = 3.5 Hz, 1H); 9.92 (NCH, d, <sup>3</sup>J = 3.5 Hz, 1H) and 11.19 (NCHN, s, 1H).  $\delta_C$  (75 MHz, d<sub>6</sub>-acetone, Me<sub>4</sub>Si) 15.49 (CH<sub>3</sub>); 21.71 (CH<sub>2</sub>); 31.50 (CH<sub>2</sub>); 38.28 (NCH<sub>3</sub>); 51.84 (NCH<sub>2</sub>); 125.11 (NCH); 126.43 (NCH) and 139.38 (NCHN)<sup>94</sup>.

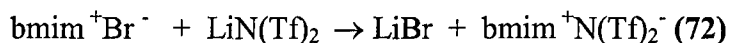
#### 5.1.4-Preparation of bmim<sup>+</sup>PF<sub>6</sub><sup>-</sup>



In this reaction hexafluorophosphoric acid (45 ml, 0.455 mol) was added dropwise using a plastic separating funnel, as some HF is formed during the reaction. Yield=92 g, 69 %

**bmim<sup>+</sup> PF<sub>6</sub><sup>-</sup> (71):**  $\delta_H$  (300 MHz, d<sub>6</sub>-acetone, Me<sub>4</sub>Si) 2.12 (CH<sub>3</sub>, t, <sup>3</sup>J = 7.5 Hz, 3H); 2.55 (CH<sub>2</sub>, m, 2H); 3.14 (CH<sub>2</sub>, m, 2H); 5.28 (NCH<sub>3</sub>, s, 3H); 5.57 (NCH<sub>2</sub>, t, <sup>3</sup>J = 7.15 Hz, 2H); 8.82 (NCH, d, <sup>3</sup>J = 3.5 Hz, 1H); 8.93 (NCH, d, <sup>3</sup>J = 3.5 Hz, 1H) and 10.05 (NCHN, s, 1H);  $\delta_C$  (75 MHz, d<sub>6</sub>-acetone, Me<sub>4</sub>Si) 15.42 (CH<sub>3</sub>); 21.72 (CH<sub>2</sub>); 34.46 (CH<sub>2</sub>); 38.35 (NCH<sub>3</sub>); 51.99 (NCH<sub>2</sub>); 125.15 (NCH); 126.53 (NCH) and 139.14 (NCHN)<sup>95</sup>.

#### 5.1.5-Preparation of bmim<sup>+</sup>(NTf)<sub>2</sub><sup>-</sup>



One equivalent of *N*-Lithiotrifluoromethanesulfonimide (66.34 g, 0.232 mol) was dissolved in water (50 ml) and added to the flask. Yield = 58 g, 88 %.

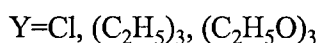
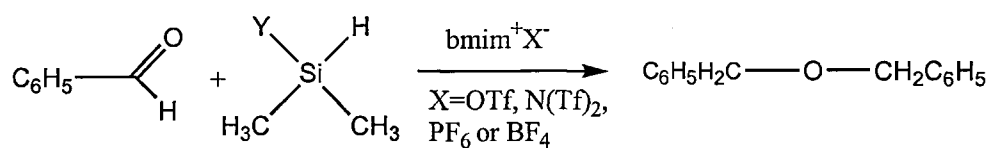
**bmim<sup>+</sup>(NTf)<sub>2</sub><sup>-</sup> (72) :**  $\delta_H$  (300 MHz, d<sub>6</sub>-acetone, Me<sub>4</sub>Si) 2.33 (CH<sub>3</sub>, t, <sup>3</sup>J = 7.4 Hz, 3H); 2.76 (CH<sub>2</sub>, m, 2H); 3.40 (CH<sub>2</sub>, m, 2H); 5.46 (NCH<sub>3</sub>, s, 3H); 5.74 (NCH<sub>2</sub>, t, <sup>3</sup>J = 7.3 Hz, 2H); 9.07 (NCH, d, <sup>3</sup>J = 3.48 Hz, 1H); 9.15 (NCH, d, <sup>3</sup>J = 3.48 Hz, 1H) and 10.39 (NCHN, s, 1H);  $\delta_C$  (75 MHz, d<sub>6</sub>-acetone, Me<sub>4</sub>Si) 15.38 (CH<sub>3</sub>); 21.74 (CH<sub>2</sub>); 34.53 (CH<sub>2</sub>); 38.44 (NCH<sub>3</sub>); 52.05 (NCH<sub>2</sub>); 125.19 (NCH); 120.67 (CF<sub>3</sub>); 124.97(NCH) and 126.61 (NCHN)<sup>68</sup>

## 5.2-Reactions of aldehydes with silanes in the presence of ionic liquids.

The ionic liquid was dried under vacuum at 50 °C before use in this reaction.

The ionic liquid (5 ml) was mixed with aldehyde (0.5 g). Two equivalents of the silane were then added *via* syringe; since the silane did not dissolve in the ionic liquid this gave a two phase reaction. During the reaction the two layers were vigorously stirred, allowing interaction of the silane with the substrate. The reaction was followed by gas-chromatography and once the reaction was complete the stirring was stopped. The mixture was separated into 2 layers, one containing the product and the other containing the remaining substrate and the promoter of the reaction. The reactions usually occurred over 12 h at room temperature. Separation was carried out by simple decantation and the catalyst solution (in the ionic liquid) could be reused immediately.

### 5.2.1-Reduction of benzaldehyde.



The reaction was carried out using  $\text{Me}_2\text{HSiCl}$  or  $(\text{EtO})_3\text{SiH}$  as silanes. At the end of the reaction the mixture had a salmon colour when using  $\text{Me}_2\text{HSiCl}$  and a pale yellow colour when using  $(\text{EtO})_3\text{SiH}$ .

The product of these reactions was shown to be dibenzyl ether based on the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The NMR spectral data were identical to the literature values<sup>40</sup>.

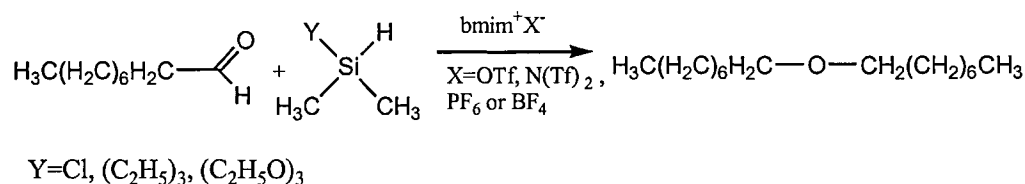


A similar reaction was carried out using  $\text{Et}_3\text{SiH}$ . At the end of the reaction the mixture had a pale yellow colour. The product was analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and shown to be the corresponding benzyl alcohol<sup>186</sup>.

With the other two ionic liquids ( $\text{X}=\text{BF}_4$  or  $\text{PF}_6$ ), the mixture remained colourless with all three silanes and the signals observed from the gas-chromatography showed the presence of only the starting materials, suggesting that no reaction had occurred in these two ionic liquids.

Similar results were observed when using the other aldehydes.

### 5.2.2-Reduction of octanal.

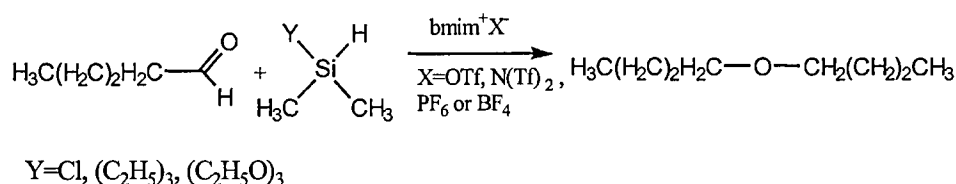


The reaction was carried out using  $\text{Me}_2\text{HSiCl}$  or  $(\text{EtO})_3\text{SiH}$  as silanes.

The products were analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy which for reaction with both silanes showed the presence of only the corresponding dioctyl ether<sup>44</sup>.

Repeating the reaction using  $\text{Et}_3\text{SiH}$  (7.8 mmol) afforded the corresponding octanol<sup>187</sup>.

### 5.2.3-Reduction of butanal

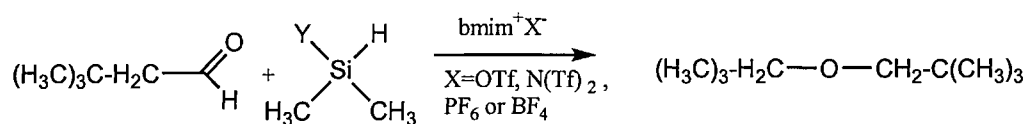


The reaction was carried out using  $\text{Me}_2\text{HSiCl}$  or  $(\text{EtO})_3\text{SiH}$  as silanes.

The products were analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy which for reaction with both silanes showed only the presence of were shown to give the corresponding dibutyl ether<sup>50</sup>.

Repeating the reaction using  $\text{Et}_3\text{SiH}$  as the silane gave the corresponding butanol<sup>188</sup>.

#### 5.2.5-Reduction of trimethylacetaldehyde.



$\text{Y}=\text{Cl}, (\text{C}_2\text{H}_5)_3, (\text{C}_2\text{H}_5\text{O})_3$

The reaction was carried out using  $\text{Me}_2\text{HSiCl}$  or  $(\text{OEt})_3\text{SiH}$  as silanes.

The products were analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy which for reaction with both silanes showed the presence of only the corresponding bis-(2,2-dimethylpropyl) ether<sup>46</sup>.

Repeating the reaction using  $\text{Et}_3\text{SiH}$  afforded the corresponding alcohol 2,2-dimethylpropanol<sup>189</sup>.

### 5.3-Reactions of silanes with ionic liquids

The silane (2 g) was mixed with 5 ml of the ionic liquid under different conditions:

- 1) Stirring overnight at 60 °C: MeHSi(OEt)<sub>2</sub>; MeSi(OEt)<sub>3</sub>; Me<sub>2</sub>Si(OEt)<sub>2</sub>; (EtO)<sub>3</sub>Si[(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>]; (EtO)<sub>3</sub>Si C<sub>6</sub>H<sub>5</sub>; (EtO)<sub>3</sub>Si CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>; CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Si(OMe)<sub>3</sub>; *cyclo*C<sub>5</sub>H<sub>10</sub>Si(OMe)<sub>3</sub>.
- 2) Using ultrasound overnight: (MeHSi(OEt)<sub>2</sub>; Me<sub>2</sub>Si(OEt)<sub>2</sub>)

#### 5.3.1-Reaction of MeHSi(OEt)<sub>2</sub> with bmim<sup>+</sup>X<sup>-</sup> where X=OTf, N(Tf)<sub>2</sub>

MeHSi(OEt)<sub>2</sub> and bmim<sup>+</sup>X<sup>-</sup> (where X=OTf, N(Tf)<sub>2</sub>) were stirred overnight at 60 °C then analysed by <sup>29</sup>Si NMR spectroscopy. The products were the linear disiloxanes: D<sub>2</sub>, D<sub>3</sub>(**39**) and D<sub>4</sub>(**40**)

δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si): 0.01 (SiCH<sub>3</sub>, s, 3H), 1.11 (CH<sub>3</sub>CH<sub>2</sub>OSi, t, 3H), 3.59 (CH<sub>3</sub>CH<sub>2</sub>OSi, q, 2H), 4.38 (SiH, s, 1H); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -0.48 (SiCH<sub>3</sub>), 23.28 (CH<sub>3</sub>CH<sub>2</sub>OSi), 58.76 (CH<sub>3</sub>CH<sub>2</sub>OSi); δ<sub>Si</sub> (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -25.56 (D<sub>2</sub>), -25.47 and -34.65 (D<sub>3</sub>), -25.83, -34.95 (D<sub>4</sub>)

MeHSi(OEt)<sub>2</sub> and bmim<sup>+</sup>X<sup>-</sup> (where X=OTf, N(Tf)<sub>2</sub>) were mixed and exposed to ultrasound overnight then analysed by <sup>29</sup>Si NMR spectroscopy. The products were the linear and also cyclic disiloxanes D<sub>3</sub>(**41**) and D<sub>4</sub>(**42**).

δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si): -0.058 (SiCH<sub>3</sub>, s, 3H) and 4.39 (SiH, s, 1H); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -0.49 (SiCH<sub>3</sub>). δ<sub>Si</sub> (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -22.36 (D<sub>3</sub>), -32.3 (D<sub>4</sub>).

### 5.3.2-Reaction of $\text{Me}_2\text{Si}(\text{OEt})_2$ with $\text{bmim}^+\text{X}^-$ where $\text{X}=\text{OTf}$ , $\text{N}(\text{Tf})_2$ .

$\text{Me}_2\text{Si}(\text{OEt})_2$  and  $\text{bmim}^+\text{X}^-$  (where  $\text{X}=\text{OTf}$ ,  $\text{N}(\text{Tf})_2$ ) were stirred overnight at 60 °C then analysed by  $^{29}\text{Si}$  NMR spectroscopy. The products were the linear disiloxanes  $\text{D}_2$ ,  $\text{D}_3$  (**43**) and  $\text{D}_4$  (**44**):

$\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ): -0.01 ( $\text{SiCH}_3$ , s, 7H), 1.15 ( $\text{OCH}_2\text{CH}_3$ , t, 3H) and 3.65 ( $\text{OCH}_2\text{CH}_3$ , q, 2H);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 1.5 ( $\text{SiCH}_3$ ), 18.99 ( $\text{OCH}_2\text{CH}_3$ ) and 58.47 ( $\text{OCH}_2\text{CH}_3$ ).  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) -12.51 ( $\text{D}_2$ ), -12.67 and -21.61 ( $\text{D}_3$ ), -12.71 and -21.8 ( $\text{D}_4$ )

$\text{Me}_2\text{Si}(\text{OEt})_2$  and  $\text{bmim}^+\text{X}^-$  (where  $\text{X}=\text{OTf}$ ,  $\text{N}(\text{Tf})_2$ ) were mixed and exposed to ultrasound overnight then analysed by  $^{29}\text{Si}$  NMR spectroscopy. The products were the linear and cyclic disiloxanes  $\text{D}_2$ ,  $\text{D}_3$ (**43**) and (**45**),  $\text{D}_4$ (**44**) and (**46**).

$\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ): -0.02 ( $\text{SiCH}_3$ , s, 24H), 1.18 ( $\text{OCH}_2\text{CH}_3$ , t, 9H) and 3.64 ( $\text{OCH}_2\text{CH}_3$ , q, 6H);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) -1.60 ( $\text{CH}_3\text{Si}$  cyclic), 0.025 ( $\text{CH}_3\text{Si}$  linear), 19.38 ( $\text{OCH}_2\text{CH}_3$ ) and 58.86 ( $\text{OCH}_2\text{CH}_3$ );  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) -12.51( $\text{D}_2$ ), -12.67 and -21.61 ( $\text{D}_3$ ), -12.71 and -21.80 ( $\text{D}_4$ ), -8.24 (*cyclic* $\text{D}_3$ ), -19.03 (*cyclic* $\text{D}_4$ )

### 5.3.3-Reaction of $\text{MeSi}(\text{OEt})_3$ with $\text{bmim}^+\text{X}^-$ where $\text{X}=\text{OTf}$ , $\text{N}(\text{Tf})_2$

$\text{MeSi}(\text{OEt})_3$  and  $\text{bmim}^+\text{X}^-$  (where  $\text{X}=\text{OTf}$ ,  $\text{N}(\text{Tf})_2$ ) were stirred overnight at 60 °C then analysed by  $^{29}\text{Si}$  NMR spectroscopy. The products were the linear disiloxanes  $\text{D}_2$ ,  $\text{D}_3$ (**47**),  $\text{D}_4$ (**48**).

$\delta_H$  (300 MHz,  $CDCl_3$ ,  $Me_4Si$ ): 0.01 ( $SiCH_3$ , s, 6H), 1.14 ( $OCH_2CH_3$ , t, 9H) and 3.63 ( $OCH_2CH_3$ , q, 6H);  $\delta_C$  (75 MHz,  $CDCl_3$ ,  $Me_4Si$ ) -4.47 ( $SiCH_3$ ), 18.03 ( $OCH_2CH_3$ ) and 58.02 ( $OCH_2CH_3$ );  $\delta_{Si}$  (79 MHz,  $CDCl_3$ ,  $Me_4Si$ ) -50.6( $D_2$ ), -50.8 and -58.97 ( $D_3$ ), -51 and -59.1( $D_4$ ).

#### 5.3.4-Reaction of $(EtO)_3Si[(CH_2)_5CH_3]$ with $bmim^+X^-$ where $X=OTf$ , $N(Tf)_2$

$(EtO)_3Si[(CH_2)_5CH_3]$  and  $bmim^+X^-$  (where  $X=OTf$ ,  $N(Tf)_2$ ) were stirred overnight at 60 °C then analysed by  $^{29}Si$  NMR spectroscopy. The products were the linear disiloxanes  $D_2$ ,  $D_3$  (**49**),  $D_4$  (**50**).

$\delta_H$  (300 MHz,  $CDCl_3$ ,  $Me_4Si$ ): 0.05 ( $SiCH_3$ , s, 3H), 0.09 ( $SiCH_2$ , t, 2H), 0.45 ( $OCH_2CH_3$ , t, 9H), 0.67 ( $CH_3$ , t, 3H), 0.71-0.94 ( $CH_2$ , m, 8H) and 3.50 ( $OCH_2CH_3$ , q, 6H);  $\delta_C$  (75 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 10.37 ( $SiCH_3$ ), 11.66 ( $SiCH_2$ ), 14.04 ( $CH_3$ ), 18.12 ( $OCH_2CH_3$ ), 22.59, 22.7, 31.5 and 32.61 ( $CH_2$ ) and 58.09 ( $OCH_2CH_3$ ).  $\delta_{Si}$  (79 MHz,  $CDCl_3$ ,  $Me_4Si$ ) -52.5 ( $D_2$ ), -53.5 and -62.8 ( $D_3$ ), -53.7 and -70 ( $D_4$ )

#### 5.3.5-Reaction of $(EtO)_3SiC_6H_5$ with $bmim^+X^-$ where $X=OTf$ , $N(Tf)_2$

$(EtO)_3SiC_6H_5$  and  $bmim^+X^-$  (where  $X=OTf$ ,  $N(Tf)_2$ ) were stirred overnight at 60 °C then analysed by  $^{29}Si$  NMR spectroscopy. The products were the linear disiloxanes  $D_2$ ,  $D_3$  (**51**),  $D_4$  (**52**).

$\delta_H$  (300 MHz,  $CDCl_3$ ,  $Me_4Si$ ): 0.91 ( $OCH_2CH_3$ , t, 9H), 3.42 ( $OCH_2CH_3$ , q, 6H) and 7.01 - 7.28 (5H, m, Ph);  $\delta_C$  (75 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 18.09 ( $OCH_2CH_3$ ),

58.64 (OCH<sub>2</sub>CH<sub>3</sub>), 127.67, 130.17, 134.55 and 134.77 (Ph).  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -65.85(D<sub>2</sub>), -66.2 and -74.9(D<sub>3</sub>), -66.4 and -75.1(D<sub>4</sub>)

### 5.3.6-Reaction of (EtO)<sub>3</sub>SiCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> with bmim<sup>+</sup>X<sup>-</sup> where X=OTf, N(Tf)<sub>2</sub>

(EtO)<sub>3</sub>SiCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> and bmim<sup>+</sup>X<sup>-</sup> (where X=OTf, N(Tf)<sub>2</sub>) stirred overnight at 60 °C then analysed by <sup>29</sup>Si NMR spectroscopy. The products were the linear disiloxanes D<sub>2</sub>, D<sub>3</sub>(**53**), D<sub>4</sub>(**54**).

$\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si): 0.82 (OCH<sub>2</sub>CH<sub>3</sub>, t, 6H), 1.29 (CH<sub>2</sub>Ph, s, 4H), 3.67 (OCH<sub>2</sub>CH<sub>3</sub>, q, 6H) and 7.14 (Ph, m, 10H);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.00 (SiCH<sub>2</sub>), 18.08 (OCH<sub>2</sub>CH<sub>3</sub>), 58.41 (OCH<sub>2</sub>CH<sub>3</sub>), 127.47, 128.04, 128.88 and 137.48 (Ph);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -59.4 (D<sub>2</sub>), -59.8 and -70.3 (D<sub>3</sub>), -59.6 and -70.1 (D<sub>4</sub>).

### 5.3.7-Reaction of CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Si(OMe)<sub>3</sub> with bmim<sup>+</sup>X<sup>-</sup> where X=OTf, N(Tf)<sub>2</sub>

CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Si(OMe)<sub>3</sub> and bmim<sup>+</sup>X<sup>-</sup> (where X=OTf, N(Tf)<sub>2</sub>) were stirred overnight at 60 °C then analysed by <sup>29</sup>Si NMR spectroscopy. The products were the linear disiloxanes D<sub>2</sub>, D<sub>3</sub>(**55**), D<sub>4</sub>(**56**).

$\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si): 1.21 (CH<sub>3</sub>, s, 3H), 3.48 (OCH<sub>3</sub>, s, 6H), 7.10 (CH=, d, 2H) and 7.44 (CH=, d, 2H);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 19.23 (CH<sub>3</sub>), 50.46 (OCH<sub>3</sub>), 122.1, 128.56, 134.3 and 140.35 (C<sub>6</sub>H<sub>4</sub>);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -62.6 (D<sub>2</sub>), -63 and -73.9 (D<sub>3</sub>), -62.8 and -72.7 (D<sub>4</sub>).

### 5.3.8-Reaction of *cyclo*-C<sub>5</sub>H<sub>10</sub>Si(OMe)<sub>3</sub> with bmim<sup>+</sup>X<sup>-</sup> where X=OTf, N(Tf)<sub>2</sub>

*cyclo*-C<sub>5</sub>H<sub>10</sub>Si (OMe)<sub>3</sub> and bmim<sup>+</sup>X<sup>-</sup> (where X=OTf, N(Tf)<sub>2</sub>) were stirred overnight at 60 °C then analysed by <sup>29</sup>Si NMR spectroscopy. The products were the linear disiloxanes D<sub>2</sub>, D<sub>3</sub> (**57**), D<sub>4</sub> (**58**).

δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si): 1.73 (SiCH, t, 2H), 2.05 (CH<sub>2</sub>, m, 12H), 2.56 (CH<sub>2</sub>, m, 4H) and 4.35 (OCH<sub>3</sub>, s, 9H); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 13.17 (SiCH), 26.73 (CH<sub>2</sub>), 27.22 (CH<sub>2</sub>) and 49.74 (OCH<sub>3</sub>); δ<sub>Si</sub> (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -51.8 (D<sub>2</sub>), -52.1 and -61.5 (D<sub>3</sub>), -52.3 and -61.7 (D<sub>4</sub>).

### 5.4-Reactions of alkoxysilanes with aldehydes in the presence of ionic liquids.

The ionic liquids were dried under vacuum at 50 °C before being used in the reaction. The ionic liquid (5 ml) was mixed with the aldehyde (0.5 g) and one equivalent of alkoxysilane R<sub>2</sub>HSi(OR') was added into the mixture. Since the alkoxyhydrosilane did not dissolve in the ionic liquid this gave a two phase reaction. During the reaction the two layers were vigorously stirred, allowing interaction of the silane with the substrate. The reaction was followed by gas-chromatography, and once the reaction was complete the stirring was stopped and the mixture separated into 2 layers, one containing the product and the other containing the remaining substrate and the promoter of the reaction. The reactions occurred over 12 h at room temperature. Separation was carried out by simple decantation and the catalyst solution (in the ionic liquid) could be reused immediately.

5.4.1-Reduction of benzaldehyde with  $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$  in ionic liquids.

The reaction using benzaldehyde and  $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$  gave a pale salmon coloured reaction mixture when  $\text{X}=\text{OTf}$ ,  $\text{N}(\text{Tf})_2$  was used as the ionic liquid . The product was analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and shown to be the corresponding benzyl octyl ether. NMR spectroscopic data were identical to the literature values<sup>190</sup>. Yield= 1.8 g, 87-88 %

5.4.2- Reduction of benzaldehyde with  $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$  in ionic liquids.

The reaction using benzaldehyde and  $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$  gave a pale salmon coloured reaction mixture when  $\text{X}=\text{OTf}$ ,  $\text{N}(\text{Tf})_2$  was used as the ionic liquid . The product was analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and shown to be the corresponding benzyl butyl ether. NMR spectroscopy data were identical to the literature values<sup>53</sup>. Yield=1.45 g, 92-96 %

5.4.3-Reduction of butanal with  $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$  or octanal with  $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$  in ionic liquids.

The reaction was repeated using octanal and  $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$  or butanal and  $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$ . The product was analysed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and shown to be the corresponding butyl octyl ether. NMR spectroscopic data were identical to the literature values<sup>53</sup>. Yield= 1.51 g, 86 % when reacting octanal with  $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$  and 1.4 g, 80 % when reacting butanal with  $\text{Me}_2\text{HSiO}(\text{CH}_2)_7\text{CH}_3$ .



#### 5.4.4-Reduction of trimethylacetaldehyde and $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$ .

Trimethylacetaldehyde and one equivalent of  $\text{Me}_2\text{HSiO}(\text{CH}_2)_3\text{CH}_3$  (0.85 g) were reacted to give the corresponding butyl (2,2-dimethylpropyl) ether. NMR spectroscopic data were identical to the literature values<sup>55</sup>. Yield=1.32 g, 57 %

#### 5.5-Hydrosilylation of alkenes in ionic liquids.

Alkene (5.94 mmol) was stirred with ionic liquid (2ml)  $\text{bmim}^+\text{X}^-$  (where  $\text{X}^- = \text{OTf}, \text{N}(\text{Tf})_2, \text{BF}_4$  and  $\text{PF}_6$ ). Then one equivalent of triethoxysilane (5.9 mmol) was added followed by  $10\mu\text{l}$  of chloroplatinic acid (0.2 mol/l in isopropanol). The mixture was then refluxed at  $60^\circ\text{C}$ , under nitrogen, for 24 h. The organic and ionic liquid layers were separated by simple decantation. The organic solvent was removed under vacuum.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy were used to analyse the product obtained.

##### 5.5.1-Hydrosilylation of 1-hexene.

1-Hexene (5.94mmol) and triethoxysilane (5.9 mmol) afforded an isolated yield of the  $\alpha$ - and  $\beta$ - product of 0.47 g, 40 %, and the ratio  $\alpha$ : $\beta$  was 52:48 from NMR spectroscopy of the crude product.

Mixture of **triethoxyhexylsilane**  $[\text{CH}_3\text{CH}_2\text{O}]_3\text{Si}[(\text{CH}_2)_5\text{CH}_3]$  (**77**):  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.59 (2H, t,  $^3\text{J} = 6.6$  Hz,  $\text{RCH}_2\text{Si}$ ), 0.84 (3H, t,  $^3\text{J} = 6.4$  Hz), 1.15-1.38 (17H, m,  $4\times\text{CH}_2$  and  $3\times\text{SiOCH}_2\text{CH}_3$ ) and 3.83 (6H, q,  $^3\text{J} = 7$  Hz,  $3\times\text{SiOCH}_2$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ); 10.24 ( $\text{RCH}_2\text{Si}$ ), 11.05 ( $\text{CH}_2\text{CH}_3$ ),

17.81 (SiOCH<sub>2</sub>CH<sub>3</sub>), 18.01, 22.41, 22.71, 32.71 (4× CH<sub>2</sub>) and 57.99 (SiOCH<sub>2</sub>),  
δ<sub>Si</sub> (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -44.63.

and triethoxy(1-methylpentyl)silane [CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[CH(CH<sub>3</sub>)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]

(76): δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.63 (1H, m, RCHSi), 0.78 (3H, d, <sup>3</sup>J = 6.4 Hz, CH<sub>3</sub>), 1.1-1.3 (15H, m, 3×CH<sub>2</sub> and 3×SiOCH<sub>2</sub>CH<sub>3</sub>); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 10.88 (RCHSi), 17.89 (SiOCH<sub>2</sub>CH<sub>3</sub>), 18.09 (SiOCH<sub>2</sub>CH<sub>3</sub>), 22.58, 25.45, 31.37 (3× CH<sub>2</sub>) and 58.1 (SiOCH<sub>2</sub>), δ<sub>Si</sub> (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -44.86

The reaction was repeated using 1-hexene and triethylsilane. The isolated yield of the α- and β- product was 0.39 g, 33 % and the ratio α:β was 50:50 from NMR spectroscopy of the crude product.

Mixture of triethylhexylsilane [CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>] (59): δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.49 (2H, t, <sup>3</sup>J = 6.7 Hz, SiCH<sub>2</sub>R), 0.56 (6H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 0.89 (9H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 0.97 (3H, t, 3J = 6.5 Hz, CH<sub>3</sub>), 1.2-1.38 (8H, m, 4×CH<sub>2</sub>); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.28 (SiCH<sub>2</sub>CH<sub>3</sub>), 5.71 (SiCH<sub>2</sub>R), 12.3 (SiCH<sub>2</sub>CH<sub>3</sub>), 15.86 (CH<sub>3</sub>), 22.44, 25.08, 27.31 and 29.5 (4×CH<sub>2</sub>); δ<sub>Si</sub> (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 6.65

and triethyl(1-methylpentyl)silane [CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>Si[CH(CH<sub>3</sub>)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>] (60):

δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.55 (1H, m, SiCHR), 0.64 (6H, m, 3× SiCH<sub>2</sub>CH<sub>3</sub>), 0.90 (9H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 1.18-1.35 (6H, m, 3×CH<sub>2</sub>), 1.41 (3H, d, <sup>3</sup>J = 7 Hz, CH<sub>3</sub>), 1.49 (3H, t, <sup>3</sup>J = 6.8 Hz, CH<sub>3</sub>); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.67 (SiCH<sub>2</sub>CH<sub>3</sub>), 7.23 (SiCHR), 14.50 (SiCH<sub>2</sub>CH<sub>3</sub>), 16.39 (CH<sub>3</sub>), 17.87 (CH<sub>3</sub>), 24.06, 25.52 and 27.99 (3× CH<sub>2</sub>); δ<sub>Si</sub> (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 8.87

### 5.5.2-Hydrosilylation of styrene.

Styrene (4.8mmol) was subjected to the same reaction using triethoxysilane (4.8mmol).  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy were used to analyse the product obtained.

The isolated yield of the  $\alpha$ - and  $\beta$ - product was 0.25 g, 29 % and the ratio  $\alpha$ : $\beta$  was 55:45 from  $^1\text{H}$  NMR spectroscopy of the crude product.

**Triethoxyphenethylsilane  $[\text{CH}_3\text{CH}_2\text{O}]_3\text{Si}[(\text{CH}_2)_2\text{Ph}]$  (79):**  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.82 (2H, t,  $^3J = 6.9$  Hz,  $\text{SiCH}_2$ ), 1.05 (9H, m,  $3 \times \text{SiOCH}_2\text{CH}_3$ ), 2.61 (2H, t,  $^3J = 6.9$  Hz,  $\text{CH}_2\text{Ph}$ ), 3.58 (6H, m,  $3 \times \text{SiOCH}_2$ ) and 7.02-7.17 (Ph);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 12.44 ( $\text{SiCH}_2$ ), 18.18 ( $\text{SiOCH}_2\text{CH}_3$ ), 25.31 ( $\text{CH}_2\text{Ph}$ ), 28.89 ( $\text{SiOCH}_2$ ) and 113.61, 126.80, 128.19, 136.79 (Ph);  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) -45.99.

and  **$[\text{CH}_3\text{CH}_2\text{O}]_3\text{Si}[\text{CH}(\text{CH}_3)\text{Ph}]$  (78):**  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.87 (1H, q,  $^3J = 7.2$  Hz,  $\text{SiCHR}$ ), 1.12 (9H, m,  $3 \times \text{SiOCH}_2\text{CH}_3$ ), 1.32 (3H, d,  $^3J = 7.2$  Hz,  $\text{CH}_3$ ), 3.69 (6H, m,  $3 \times \text{SiOCH}_2$ ) and 7.1-7.29 (Ph);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 15.49 ( $\text{SiCH}$ ), 17.90 ( $\text{CH}_3$ ), 18.28 ( $\text{SiOCH}_2\text{CH}_3$ ), 25.44 ( $\text{SiOCH}_2$ ) and 125.47, 127.68, 128.39, 144.51 (Ph);  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) -46.6.

Repeating the reaction using styrene (4.8 mmol) and triethylsilane (4.8 mmol) gave an isolated yield of the  $\alpha$ - and  $\beta$ - product of 0.31 g, 23 % and the ratio  $\alpha$ : $\beta$  was 60:40 from  $^1\text{H}$  NMR spectroscopy of the crude product.

**Triethylphenethylsilane  $[\text{CH}_3\text{CH}_2]_3\text{Si}[(\text{CH}_2)_2\text{Ph}]$  (61):**  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.54 (6H, m,  $3 \times \text{SiCH}_2\text{CH}_3$ ), 0.61 (2H, t,  $^3J = 6.7$  Hz,  $\text{SiCH}_2\text{R}$ ), 0.94 (9H,

m,  $3\times\text{SiCH}_2\text{CH}_3$ ), 1.10 (2H, t,  $^3J = 6.7$  Hz,  $\text{CH}_2\text{Ph}$ ) and 7.13-7.32 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 2.48 ( $\text{SiCH}_2\text{CH}_3$ ), 2.81 ( $\text{SiCH}_2\text{R}$ ), 8.1 ( $\text{SiCH}_2\text{CH}_3$ ), 25.31 ( $\text{CH}_2\text{Ph}$ ) 113.64, 127.76, 129.8 and 136.92 ( $4\times\text{C}$  aromatic);  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 6.89

and **[CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>Si[CH(CH<sub>3</sub>)Ph] (62)**:  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.59 (6H, m,  $3\times\text{SiCH}_2\text{CH}_3$ ), 0.84 (1H, q,  $^3J = 6.5$  Hz,  $\text{SiCHR}$ ), 0.99 (9H, m,  $3\times\text{SiCH}_2\text{CH}_3$ ), 1.13 (3H, d,  $^3J = 6.5$  Hz,  $\text{CH}_3$ ) and 7.16-7.35 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 2.67 ( $\text{SiCH}_2\text{CH}_3$ ), 2.93 ( $\text{SiCHR}$ ), 8.31 ( $\text{SiCH}_2\text{CH}_3$ ), 25.86 ( $\text{CHPh}$ ), 114.45, 126.02, 128.48 and 137.61 (Ph);  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 6.71

### 5.5.3-Hydrosilylation of the allyl butyl ether.

The reactions were repeated using allyl butyl ether (4.4 mmol) and triethoxysilane or triethylsilane (4.4 mmol). The isolated yield of the  $\alpha$ - and  $\beta$ -product was 0.58 g, 48 % for  $(\text{EtO})_3\text{SiH}$  (ratio  $\alpha:\beta$  was 50:50) and 0.39 g, 39 % for  $\text{Et}_3\text{SiH}$  (ratio  $\alpha:\beta$  was 60:40).

#### **3-(Butoxypropyl)triethoxysilane[CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>3</sub>O(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>] (81):**

$\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.37 (2H, t,  $^3J = 7.4$  Hz,  $\text{SiCH}_2\text{R}$ ), 0.66 (3H, q,  $^3J = 6.9$  Hz,  $\text{CH}_3$ ), 0.71-1.08 (15H, m,  $3\times\text{CH}_2$  and  $3\times\text{SiOCH}_2\text{CH}_3$ ), 3.28 (2H, t,  $^3J = 7$  Hz,  $\text{OCH}_2$ ), 3.32 (6H, m,  $3\times\text{SiOCH}_2$ ) and 3.37 (2H, t,  $^3J = 7$  Hz,  $\text{OCH}_2$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 5.98 ( $\text{SiCH}_2\text{R}$ ), 17.98 ( $\text{CH}_3$ ), 18.26 ( $\text{SiOCH}_2\text{CH}_3$ ), 23.00 ( $\text{CH}_2$ ), 23.60 ( $\text{CH}_2$ ), 24.05 ( $\text{CH}_2$ ), 58.33 ( $\text{SiOCH}_2$ ), 70.52 ( $\text{OCH}_2$ ) and 73.08 ( $\text{OCH}_2$ );  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) -42.83

and  $[\text{CH}_3\text{CH}_2\text{O}]_3\text{Si}[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}(\text{CH}_2)_3\text{CH}_3]$  (80):  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.43 (1H, m, SiCH), 0.63 (3H, t,  $^3J = 7$  Hz,  $\text{CH}_3$ ), 0.67-1.1 (16H, m,  $\text{CH}_3$ ,  $2\times\text{CH}_2$ ,  $3\times\text{SiOCH}_2\text{CH}_3$ ), 3.25 (2H, d,  $^3J = 7.2$  Hz,  $\text{OCH}_2$ ), 3.36 (6H, m,  $3\times\text{SiOCH}_2$ ) and 3.40 (2H, t,  $^3J = 6.9$  Hz,  $\text{OCH}_2\text{R}$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 6.39 (SiCHR), 13.09 ( $\text{CH}_3$ ), 18.08 ( $\text{CH}_3$ ), 19.35 ( $\text{SiOCH}_2\text{CH}_3$ ), 25.50 ( $\text{CH}_2$ ), 31.87 ( $\text{CH}_2$ ), 59.12 ( $\text{SiOCH}_2$ ), 70.58 ( $\text{OCH}_2$ ) and 74.09 ( $\text{OCH}_2$ );  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) -46.16

**3-(Butoxypropyl)triethylsilane** $[\text{CH}_3\text{CH}_2]_3\text{Si}[(\text{CH}_2)_3\text{O}(\text{CH}_2)_3\text{CH}_3]$  (64):  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.05 (2H, m,  $\text{SiCH}_2\text{R}$ ), 0.09 (6H, m,  $3\times\text{SiCH}_2$ ), 0.38 (9H, m,  $3\times\text{SiCH}_2\text{CH}_3$ ), 0.85-0.98 (4H, m,  $2\times\text{CH}_2$ ), 1.03 (3H, t,  $^3J = 6.8$  Hz,  $\text{CH}_3$ ), 2.87 (4H, t,  $^3J = 7.2$  Hz,  $2\times\text{OCH}_2$ ) and 2.92 (2H, t,  $^3J = 7.2$  Hz,  $\text{OCH}_2$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 2.39 ( $\text{SiCH}_2\text{R}$ ), 3.20 ( $\text{SiCH}_2$ ), 8.06 ( $\text{SiCH}_2\text{CH}_3$ ), 13.86 ( $\text{CH}_3$ ), 19.40 ( $\text{CH}_2$ ), 25.80 ( $\text{CH}_2$ ), 62.29 ( $\text{OCH}_2$ ) and 70.54 ( $\text{OCH}_2$ );  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 7.13

and  $[\text{CH}_3\text{CH}_2]_3\text{Si}[\text{CH}(\text{CH}_3)(\text{CH}_2)_2\text{O}(\text{CH}_2)_3\text{CH}_3]$  (63):  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.11 (6H, m,  $3\times\text{SiCH}_2$ ), 0.42 (9H, m,  $3\times\text{SiCH}_2\text{CH}_3$ ), 0.61 (1H, m, SiCH), 0.72 (3H, d,  $^3J = 6.3$  Hz,  $\text{CH}_3$ ), 0.87-0.93 (4H, m,  $2\times\text{CH}_2$ ), 1.06 (3H, t,  $^3J = 6.8$  Hz,  $\text{CH}_3$ ), 2.82 (1H, q,  $^3J = 7.14$  Hz, CHO) and 3.07 (2H, t,  $^3J = 6.6$  Hz,  $\text{OCH}_2$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 3.37 ( $\text{SiCH}_2$ ), 8.98 ( $\text{SiCH}_2\text{CH}_3$ ), 10.83 ( $\text{CH}_3$ ), 13.82 ( $\text{CH}_3$ ), 19.33 ( $\text{CH}_2$ ), 24.02 ( $\text{CH}_2$ ), 31.86 ( $\text{SiCHO}$ ) and 74.05 ( $\text{OCH}_2$ );  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 8.79

#### 5.5.4-Hydrosilylation of allyl phenyl ether.

Allyl phenyl ether (3.73 mmol) and triethoxysilane or triethylsilane (3.73 mmol) were reacted to give an isolated yield of the  $\alpha$ - and  $\beta$ - product of 0.6 g, 53 % for  $(\text{EtO})_3\text{SiH}$  (ratio  $\alpha$ : $\beta$  was 40:60) and 0.47 g, 42 % for  $\text{Et}_3\text{SiH}$  (ratio  $\alpha$ : $\beta$  was 40:60)

**3-(Phenoxypropyl)triethoxysilane[CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>3</sub>OPh] (83):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.90 (2H, t,  $^3J = 7.4$  Hz, SiCH<sub>2</sub>R), 1.10 (9H, m, 3 $\times$ SiOCH<sub>2</sub>CH<sub>3</sub>) 1.81 (2H, m, CH<sub>2</sub>), 3.82 (2H, t,  $^3J = 6.9$  Hz, OCH<sub>2</sub>) and 6.8-7.1 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 6.42 (SiCH<sub>2</sub>), 17.79 (SiOCH<sub>2</sub>CH<sub>3</sub>), 22.72 (CH<sub>2</sub>), 58.10 (SiOCH<sub>2</sub>), 58.95 (OCH<sub>2</sub>) and 114.37, 119.17, 120.32, 121.81, 158.98 (Ph);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -45.41.

and [CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[CH(CH<sub>3</sub>)CH<sub>2</sub>OPh] (82):  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.62 (1H, m, SiCHR), 1.18 (9H, m, 3 $\times$ SiOCH<sub>2</sub>CH<sub>3</sub>), 1.32 (3H, d,  $^3J = 7.2$  Hz, CH<sub>3</sub>), 3.76 (6H, m, 3 $\times$ SiOCH<sub>2</sub>), 4.18 (2H, d,  $^3J = 7.5$  Hz, OCH<sub>2</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.69 (SiCH), 10.39 (CH<sub>3</sub>), 18.06 (SiOCH<sub>2</sub>CH<sub>3</sub>), 53.27 (SiOCH<sub>2</sub>), 59.50 (OCH<sub>2</sub>) and 114.39, 119.34, 120.45, 121.82, 159.04 (Ph);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -47.6

**3-(Phenoxypropyl)triethylsilane[CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>3</sub>OPh] (65):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.11 (6H, m, 3 $\times$ SiCH<sub>2</sub>), 0.16 (2H, t,  $^3J = 7.5$  Hz, SiCH<sub>2</sub>R), 0.71 (9H, m, 3 $\times$ SiCH<sub>2</sub>CH<sub>3</sub>), 1.28 (2H, m, CH<sub>2</sub>), 3.43 (2H, t,  $^3J = 6.97$  Hz, OCH<sub>2</sub>) and 6.37-6.74 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 2.88 (SiCH<sub>2</sub>),

3.55 (SiCH<sub>2</sub>), 7.37 (SiCH<sub>2</sub>CH<sub>3</sub>), 23.76 (CH<sub>2</sub>), 68.61 (OCH<sub>2</sub>), 114.41, 117.44, 129.35, 133.31, 158.54 (Ph);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 8.79 and [CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>Si[CH(CH<sub>3</sub>)CH<sub>2</sub>OPh] (**66**):  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.14 (6H, m, 3×SiCH<sub>2</sub>), 0.18 (1H, m, SiCHR), 0.69 (3H, d, <sup>3</sup>J = 7.2 Hz, CH<sub>3</sub>), 1.24 (9H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 3.40 (2H, d, <sup>3</sup>J = 6.9 Hz, OCH<sub>2</sub>) and 6.40-6.80 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 3.21 (SiCH<sub>2</sub>), 4.36 (SiCHR), 10.47 (SiCH<sub>2</sub>CH<sub>3</sub>), 22.56 (CH<sub>3</sub>), 70.65 (OCH<sub>2</sub>), 114.65, 120.37, 129.33, 129.47, 159.04 (Ph);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.35.

#### 5.5.5-Hydrosilylation of allyl benzene

The reaction using allyl benzene (4.2 mmol) and triethoxysilane or triethylsilane (4.2 mmol) afforded an isolated yield of the  $\alpha$ - and  $\beta$ -product of 0.45 g, 38 % for (EtO)<sub>3</sub>SiH (ratio  $\alpha$ : $\beta$  was 65:35) and 0.29 g, 30 % for Et<sub>3</sub>SiH (ratio  $\alpha$ : $\beta$  was 55:45)

**Triethoxy(3-phenylpropyl)silane**[CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>3</sub>Ph] (**85**):  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.54 (2H, t, <sup>3</sup>J = 8.2 Hz, SiCH<sub>2</sub>R), 1.16 (9H, m, 3×SiOCH<sub>2</sub>CH<sub>3</sub>), 1.61 (2H, m, CH<sub>2</sub>), 2.51 (2H, t, <sup>3</sup>J = 7.5 Hz, CH<sub>2</sub>Ph), 3.63 (6H, m, 3×SiOCH<sub>2</sub>) and 7.03-7.18 (5H, m, Ph);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si), 10.63 (SiCH<sub>2</sub>), 18.14 (SiOCH<sub>2</sub>CH<sub>3</sub>), 25.47 (CH<sub>2</sub>), 39.25 (CH<sub>2</sub>Ph), 58.31 (SiOCH<sub>2</sub>), 115.78, 126.09, 128.61, 140.08 (Ph);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -45.02 and [CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[CH(CH<sub>3</sub>)CH<sub>2</sub>Ph] (**84**):  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.74 (1H, m, SiCHR), 1.13 (9H, m, 3×SiOCH<sub>2</sub>CH<sub>3</sub>), 1.38 (3H, d, <sup>3</sup>J = 7.1 Hz, CH<sub>3</sub>), 3.24 (2H, d, <sup>3</sup>J = 7.6 Hz, CH<sub>2</sub>Ph), 3.04 (6H, m, 3×SiOCH<sub>2</sub>) and 7.03-7.18 (5H,

m, Ph);  $\delta_C$  (75 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 10.19 (SiCH), 17.96 (SiOCH<sub>2</sub>CH<sub>3</sub>), 24.87 (CH<sub>3</sub>), 40.27 (CH<sub>2</sub>Ph), 58.37 (SiOCH<sub>2</sub>), 125.69, 128.43, 137.49, 142.44 (Ph);  $\delta_{Si}$  (79 MHz,  $CDCl_3$ ,  $Me_4Si$ ) -46.18

**Triethyl(3-phenylpropyl)silane[CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>3</sub>Ph] (69):**  $\delta_H$  (300 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 0.61 (2H, m, SiCH<sub>2</sub>R), 0.88 (6H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 1.1 (9H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 1.32 (2H, m, SiCH<sub>2</sub>CH<sub>2</sub>), 2.57 (2H, t, <sup>3</sup>J = 7.1 Hz, CH<sub>2</sub>Ph) and 7.05-7.38 (5H, m, Ph);  $\delta_C$  (75 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 2.69 (SiCH<sub>2</sub>R), 3.97 (SiCH<sub>2</sub>CH<sub>3</sub>), 13.45 (SiCH<sub>2</sub>CH<sub>3</sub>), 22.71 (SiCH<sub>2</sub>CH<sub>2</sub>), 36.05 (CH<sub>2</sub>Ph), 119.20, 123.67, 125.8 and 132.19 (4×C Ph);  $\delta_{Si}$  (79 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 6.81 and [CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>Si[CH(CH<sub>3</sub>)CH<sub>2</sub>Ph] (70):  $\delta_H$  (300 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 0.76 (1H, m, SiCHR), 0.95 (6H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 1.20 (9H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 1.28 (3H, d, <sup>3</sup>J = 6.8 Hz, CH<sub>3</sub>), 2.84 (2H, d, <sup>3</sup>J = 7.1 Hz, CH<sub>2</sub>Ph) and 7.13-7.4 (5H, m, Ph);  $\delta_C$  (75 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 2.85 (SiCHR), 4.08 (SiCH<sub>2</sub>CH<sub>3</sub>), 16.11 (SiCH<sub>2</sub>CH<sub>3</sub>), 25.04 (SiCHCH<sub>3</sub>), 37.93 (CH<sub>2</sub>Ph), 120.02, 124, 127.53 and 134.01 (4×C Ph);  $\delta_{Si}$  (79 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 6.95

#### 5.5.6-Hydrosilylation of hexyl acrylate.

The reactions were repeated with hexyl acrylate (3.2 mmol) and triethoxysilane or triethylsilane (3.2 mmol) to obtain an isolated yield of the  $\alpha$ - and  $\beta$ - product of 0.38 g, 37 % for (EtO)<sub>3</sub>SiH (ratio  $\alpha$ : $\beta$ : $\beta$  oxysilylation was 30:10:60) and 0.25 g, 29 % for Et<sub>3</sub>SiH (ratio  $\alpha$ : $\beta$ : $\beta$  oxysilylation was 30:20:50).



### 3-(Triethoxysilanyl)propanoic acid hexyl ester

**[CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>] (87):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si)

0.34 (2H, t,  $^3J = 6.9$  Hz, SiCH<sub>2</sub>R), 0.72-0.99 (8H, m, 4×CH<sub>2</sub>), 1.10 (9H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 1.67 (3H, t,  $^3J = 7.3$  Hz, CH<sub>3</sub>), 2.14 (2H, t,  $^3J = 6.9$  Hz, CH<sub>2</sub>CO<sub>2</sub>), 3.85 (6H, q,  $^3J = 7.2$  Hz, 3×SiOCH<sub>2</sub>) and 4.41 (2H, t,  $^3J = 7.1$  Hz, CO<sub>2</sub>CH<sub>2</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.78 (SiCH<sub>2</sub>), 15.23 (SiCH<sub>2</sub>CH<sub>3</sub>), 18.10 (CH<sub>3</sub>), 20.5, 22.34, 23.05, 25.73 (4×CH<sub>2</sub>), 31.78 (SiCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>), 56.09 (SiOCH<sub>2</sub>), 62.3 (CO<sub>2</sub>CH<sub>2</sub>R) and 170.9 (CO<sub>2</sub>).  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) – 54.78

and **[CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[CH(CH<sub>3</sub>)CO<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>] (86):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.98-1.07 (8H, m, 4×CH<sub>2</sub>), 1.09 (1H, m, SiCHCO<sub>2</sub>), 1.15 (3H, d,  $^3J = 6.6$  Hz, SiCH(CH<sub>3</sub>)), 1.23 (9H, t,  $^3J = 7$  Hz, 3×SiOCH<sub>2</sub>CH<sub>3</sub>), 1.96 (3H, t,  $^3J = 6.7$  Hz, CH<sub>3</sub>), 4.24 (2H, t,  $^3J = 6.8$  Hz, CO<sub>2</sub>CH<sub>2</sub>) and 4.52 (6H, q,  $^3J = 7$  Hz, 3×SiOCH<sub>2</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 9.95 (SiCH), 16.47 (SiOCH<sub>2</sub>CH<sub>3</sub>), 19.4 (CH<sub>3</sub>), 21.05, 23.20, 24.73, 26.18 (4×CH<sub>2</sub>), 26.34 (SiCH(CH<sub>3</sub>)), 57.1 (SiOCH<sub>2</sub>), 64.23 (CO<sub>2</sub>CH<sub>2</sub>) and 168.60 (CO<sub>2</sub>).  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) – 48.92

and **[CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>2</sub>CH[OSi(OEt)<sub>3</sub>]O(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>] (88):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.082 (2H, t,  $^3J = 6.8$  Hz, SiCH<sub>2</sub>R), 1.12 (3H, t,  $^3J = 7$  Hz, CH<sub>3</sub>), 1.15 (18H, m, 2×[3×SiOCH<sub>2</sub>CH<sub>3</sub>]), 1.30-1.51 (8H, m, 4×CH<sub>2</sub>), 1.62 (2H, m, CH<sub>2</sub>), 3.80 (12H, m, 2×[3×SiOCH<sub>2</sub>CH<sub>3</sub>]), 3.86 (2H, t, OCH<sub>2</sub>) and 5.88 (1H, t,  $^3J = 6.9$  Hz, OCHO);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 8.39 (SiCH<sub>2</sub>R), 13.93 (CH<sub>3</sub>), 17.71 (CH<sub>2</sub>), 18.06 (SiOCH<sub>2</sub>CH<sub>3</sub>), 18.38, 22.49, 25.05, 25.39 (4×CH<sub>2</sub>),

58.31(SiOCH<sub>2</sub>), 59.11 (OCH<sub>2</sub>R) and 78.90 (OCHO);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -58.28 and -80.78

**CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>OCH(OSiEt<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiEt<sub>3</sub> (73):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.1-0.22 (14H, m, 2×Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> and Et<sub>3</sub>SiCH<sub>2</sub>), 0.64 (18H, m, 2×Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 0.71 (3H, t, <sup>3</sup>J = 7.3 Hz, CH<sub>3</sub>), 0.86-0.92 (10H, m, 5×CH<sub>2</sub>), 3.07 (2H, t, <sup>3</sup>J = 7.1 Hz, OCH<sub>2</sub>) and 5.2 (1H, t, <sup>3</sup>J = 6.9 Hz, OCHO);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.36 (SiCH<sub>2</sub>), 4.87 (OSiCH<sub>2</sub>), 9.13 (CH<sub>3</sub>), 13.88 (CH<sub>3</sub>), 22.52, 25.32, 25.79, 25.85 (4×CH<sub>2</sub>), 27.56, 27.9 (2×CH<sub>2</sub>), 31.38 (OCH<sub>2</sub>) and 80.21 (OCHO);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 6.71 (RCH<sub>2</sub>SiEt<sub>3</sub>), 16.12 (ROSiEt<sub>3</sub>)

and **[CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>SiCH(CH<sub>3</sub>)CO<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> (71):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.051 (12H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 0.53 (9H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 0.67 (3H, d, <sup>3</sup>J = 6.9 Hz, CH<sub>3</sub>), 0.78 (3H, m, CH<sub>3</sub>), 0.94-1.00 (8H, m, 4×CH<sub>2</sub>), 1.81 (1H, m, COCHSiEt) and 3.45 (2H, t, <sup>3</sup>J = 6.9 Hz, OCH<sub>2</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.68 (SiCH<sub>2</sub>), 6.69 (SiCH), 7.22 (CH<sub>3</sub>), 9.07 (CH<sub>3</sub>), 10.15 (CH<sub>3</sub>), 22.46, 24.57, 25.50, 25.81 (4×CH<sub>2</sub>) 31.63 (OCH<sub>2</sub>) and 174.53 (CO);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 8.15

and **[CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>Si(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> (72):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.065 (12H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 0.077 (2H, m, SiCH<sub>2</sub>R), 0.44 (9H, m, 3×SiCH<sub>2</sub>CH<sub>3</sub>), 0.50 (3H, m, CH<sub>3</sub>), 0.98-1.07 (8H, m, 4×CH<sub>2</sub>), 1.75 (2H, m, CH<sub>2</sub>CO) and 3.57 (2H, t, <sup>3</sup>J = 7 Hz, OCH<sub>2</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.73 (SiCH<sub>2</sub>CH<sub>3</sub>), 5.44 (SiCH<sub>2</sub>), 6.75 (SiCH<sub>2</sub>CH<sub>3</sub>), 9.52 (CH<sub>3</sub>), 21.90, 22.08, 24.17, 25.60 (4×CH<sub>2</sub>), 31.90 (OCH<sub>2</sub>) and 175.26 (CO);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 6.71

### 5.5.7-Hydrosilylation of but-3-enoic acid.

Butenoic acid (5.81 mmol) was reacted with triethoxysilane or triethylsilane (5.81 mmol) to give an isolated yield of the  $\alpha$ - and  $\beta$ - product of 0.53 g, 22 % for (EtO)<sub>3</sub>SiH ( $\alpha$ : $\beta$  ratio was 20:80) and 0.31 g, 16 % for Et<sub>3</sub>SiH ( $\alpha$ : $\beta$  ratio was 30:70).

**[CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H] (89):**  $\delta_H$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.87 (2H, m, SiCH<sub>2</sub>), 1.12 (9H, m, 3×SiOCH<sub>2</sub>CH<sub>3</sub>), 1.34 (2H, m, CH<sub>2</sub>), 2.33 (2H, t, <sup>3</sup>J = 7.5 Hz, CH<sub>2</sub>CO<sub>2</sub>) and 3.82 (6H, m, 3×SiOCH<sub>2</sub>);  $\delta_C$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.17 (SiCH<sub>2</sub>), 17.95 (SiOCH<sub>2</sub>CH<sub>3</sub>), 19.30 (CH<sub>3</sub>), 36.23 (CH<sub>2</sub>CO<sub>2</sub>), 49.90 (SiOCH<sub>2</sub>CH<sub>3</sub>) and 123.34 (CO<sub>2</sub>);  $\delta_{Si}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -45.96 and **[CH<sub>3</sub>CH<sub>2</sub>O]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CO(OSi(OCH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>)] (90):**  $\delta_H$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.43 (2H, m, SiCH<sub>2</sub>), 1.07 (18H, m, 2× [3×SiOCH<sub>2</sub>CH<sub>3</sub>]), 1.28 (2H, m, CH<sub>2</sub>), 2.53 (2H, t, <sup>3</sup>J = 7 Hz, CH<sub>2</sub>CO<sub>2</sub>) and 4.05 (12H, m, 2×[3×SiOCH<sub>2</sub>CH<sub>3</sub>]);  $\delta_C$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.10 (SiCH<sub>2</sub>R), 12.05 (CH<sub>3</sub>), 14.80 (CH<sub>2</sub>), 41.30 (CH<sub>2</sub>CO<sub>2</sub>), 52.18 (SiOCH<sub>2</sub>CH<sub>3</sub>) and 152.23 (CO);  $\delta_{Si}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -46.62, and -81.76

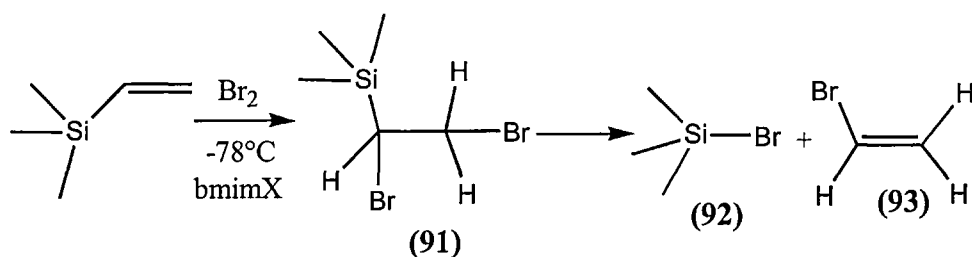
**[CH<sub>3</sub>CH<sub>2</sub>]<sub>3</sub>Si[(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>] (75):**  $\delta_H$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.46 (12H, m, 6×SiCH<sub>2</sub>), 1.11 (2H, m, CH<sub>2</sub>), 1.78 (18H, m, 6×SiCH<sub>2</sub>CH<sub>3</sub>) and 2.61 (2H, d, CH<sub>2</sub>CO<sub>2</sub>);  $\delta_C$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 3.98 (SiCHR), 4.69 and 5.24 (SiCH<sub>2</sub>), 13.47 and 13.51 (SiCH<sub>2</sub>CH<sub>3</sub>), 19.49 (CH<sub>3</sub>), 39.7 (CH<sub>2</sub>CO<sub>2</sub>) and 174.33 (CO);  $\delta_{Si}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 6.74 and 25.05

and  $[\text{CH}_3\text{CH}_2]_3\text{Si}[\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{H}]$  (**74**):  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.26 (1H, m, SiCHR), 0.42 (6H, m,  $3\times\text{SiCH}_2$ ), 0.66 (3H, d,  $^3J = 6.8$  Hz,  $\text{CH}_3$ ), 1.16 (9H, m,  $3\times\text{SiCH}_2\text{CH}_3$ ), 2.58 (2H, d,  $\text{CH}_2\text{CO}$ ) and 6.50 (COOH);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 3.12 (SiCHR), 4.29 (SiCH<sub>2</sub>), 11.12 (SiCH<sub>2</sub>CH<sub>3</sub>), 18.12 ( $\text{CH}_3$ ), 37.88 ( $\text{CH}_2\text{CO}_2$ ) and 172.03 (CO);  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 6.71

## 5.6-Other nucleophilic reactions in ionic liquids.

### 5.6.1-Bromination of silanes.

#### 5.6.1.1-Bromination of trimethylvinylsilane in ionic liquids



Trimethylvinylsilane (1 g, 10 mmol) was added to  $[\text{bmim}][\text{OTf}]$  (5 ml) and the solution cooled to  $-78^\circ\text{C}$  for 10 min. One equivalent of bromine (0.63 ml) was added dropwise to the solution, while maintaining the low temperature. After addition the mixture was kept at this temperature for a further 20 min then allowed to warm up to room temperature and stirred for 2 h.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectroscopy were used to analyse the reaction mixture and compared with literature spectra<sup>191</sup>.

**(1,2-Dibromoethyl)trimethylsilane (91):**  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.045 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 3.25 (1H, dd,  $^2J = 12$  Hz,  $^3J = 7$  Hz, BrCHR), 3.5 (1H, t,  $^3J = 7$  Hz, BrCHSiMe<sub>3</sub>) and 3.75 (1H, dd,  $^2J = 12$  Hz,  $^3J = 7$  Hz, BrCHR);  $\delta_{\text{C}}$  (75

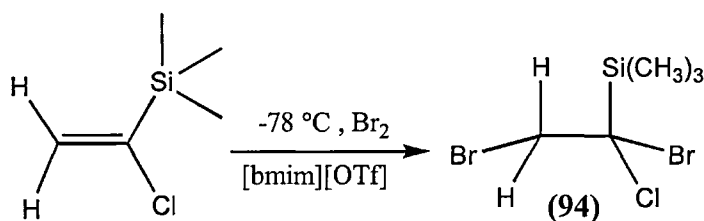
MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -2.09 (Si(CH<sub>3</sub>)<sub>3</sub>), 4.64 (BrCHSi) and 42.56 (RCH<sub>2</sub>Br);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 6.35

**Trimethylbromosilane (92):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.68 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -1.9 (Si(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{Si}}$  (79 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 27.43.

**Bromoethene (93):**  $\delta_{\text{H}}$  (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 5.46 (1H, dd,  $J_{\text{cis}} = 7.14$  Hz,  $J_{\text{gem}} = 2$  Hz), 5.71 (1H, dd,  $J_{\text{trans}} = 15$  Hz,  $J_{\text{gem}} = 2$  Hz) and 6.24 (1H, dd,  $J_{\text{cis}} = 7.14$  Hz,  $J_{\text{trans}} = 15$  Hz);  $\delta_{\text{C}}$  (75 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 114.04 (=CH<sub>2</sub>) and 122 (=CHBr).

The reaction was carried out in the same way as above, in the absence of [bmim][OTf]. <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR spectroscopy were used to analyse the reaction mixture and compared with the literature spectra. The reaction gave similar results to those observed using ionic liquids.

#### 5.6.1.2-Bromination of (1-chloro-vinyl)trimethylsilane



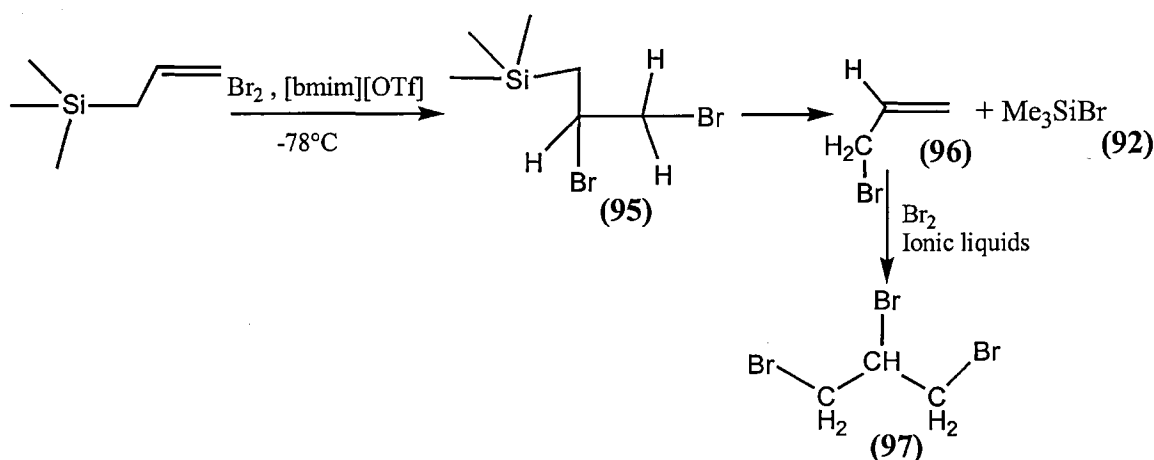
(1-Chloro-vinyl)trimethylsilane (1 g, 7.46 mmol) was added to [bmim][OTf] (5 ml), the solution was cooled to -78 °C for 10 min. One equivalent of bromine (0.9 ml) was added dropwise to the solution, while maintaining the low

temperature. After addition the mixture was kept at this temperature for a further 20 min then allowed to warm up to room temperature and stirred for 2 h.

$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectroscopy were used to analyse the reaction mixture.

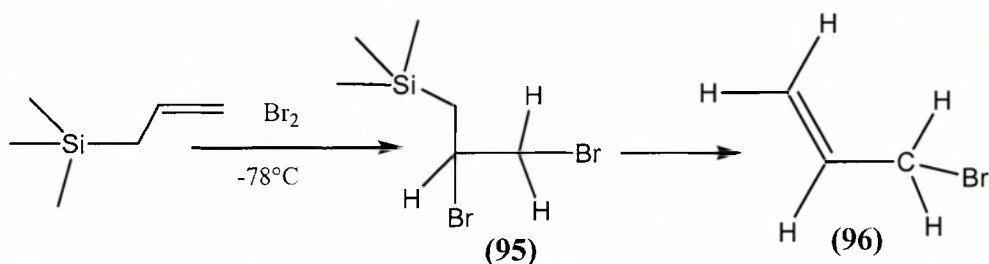
**(1-chloro-1,2-dibromoethyl)trimethylsilane (94):**  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.31 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ) and 4.12 (2H, s,  $\text{CH}_2\text{Br}$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.99 ( $\text{Si}(\text{CH}_3)_3$ ), 31.56 ( $\text{SiCCl}(\text{Br})$ ) and 44.65 ( $\text{CH}_2\text{Br}$ );  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 6.08

#### 5.6.1.3-Bromination of allyltrimethylsilane.



Allyltrimethylsilane (1g, 8.75 mmol) was added to  $[\text{bmim}][\text{OTf}]$  (5 ml), the solution was cooled to  $-78^\circ\text{C}$  for 10 min. One equivalent of bromine (1 ml) was added dropwise to the solution, while maintaining the low temperature. After addition the mixture was kept at this temperature for a further 20 min then allowed to warm up to room temperature and stirred for 2 h.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectroscopy were used to analyse the reaction mixture and compared with literature spectra<sup>192</sup>.

**1,2,3-Dibromopropane (97):**  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 3.86 (4H, d,  $^3J = 6.9$  Hz,  $2 \times \text{CH}_2\text{Br}$ ) and 4.29 (1H, m,  $\text{CHBr}$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 32.80 ( $\text{CHBr}$ ) and 34.85 ( $\text{CH}_2\text{Br}$ ).

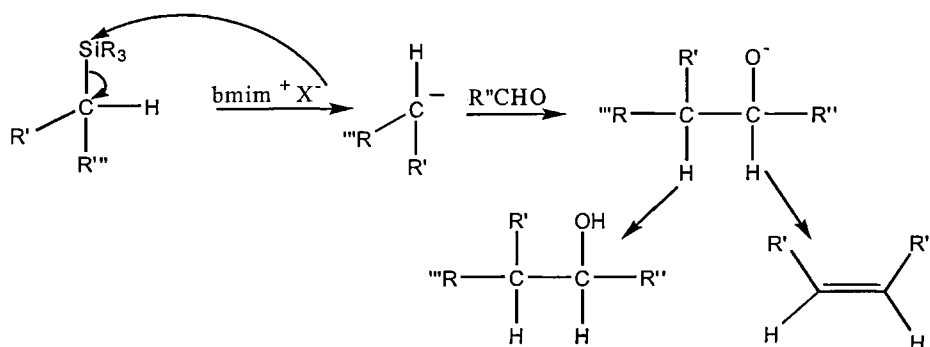


The above reaction was repeated in the absence of solvent.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy were used to analyse the reaction mixture and compared with literature spectra<sup>193</sup>.

**(2,3-Dibromopropyl)trimethylsilane (95):**  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.53 (9H, s,  $(\text{Si}(\text{CH}_3)_3)$ ), 1.81 (2H, d,  $^3J = 6.61$  Hz,  $\text{CH}_2\text{Si}$ ), 3.77 (1H, m,  $\text{CH}(\text{CH}_2)_2\text{Br}$ ) and 3.90 (2H, d,  $^3J = 6.6$  Hz,  $\text{BrCH}_2\text{R}$ );  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 1.52 ( $(\text{Si}(\text{CH}_3)_3)$ ), 4.47 ( $\text{SiCH}_2$ ), 34.81 ( $\text{RCHBr}$ ) and 48.16 ( $\text{CH}_2\text{Br}$ );  $\delta_{\text{Si}}$  (79 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 7.35 ppm.

**3-Bromopropene (96):**  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 1.75 (2H, d,  $^3J = 6.9$  Hz,  $\text{CH}_2\text{Br}$ ), 5.09 (1H, dd,  $J_{\text{gem}} = 1.3$  Hz,  $J_{\text{cis}} = 7.2$  Hz), 5.25 (1H, dd,  $J_{\text{gem}} = 1.3$  Hz,  $J_{\text{trans}} = 18$  Hz) and 6.02 (1H,  $J_{\text{cis}} = 7.2$  Hz,  $J_{\text{trans}} = 18$  Hz);  $\delta_{\text{C}}$  (75 MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 24.16 ( $\text{CH}_2\text{Br}$ ) 119.05 ( $=\text{CH}_2$ ), 134.16 ( $=\text{CHR}$ )

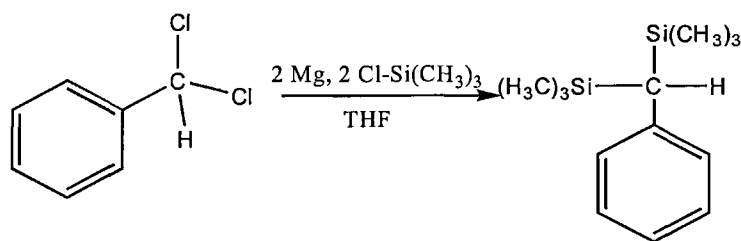
### 5.6.2-Peterson reaction.



#### 5.6.2.1-Reaction of benzyltrimethylsilane with benzaldehyde.

Benzyltrimethylsilane (1 g, 6 mmol) was mixed with of [bmim][OTf] (5 ml) and benzaldehyde (0.68 g, 6.1 mmol) was added to the mixture and stirred at room temperature for 24 h. The mixture was analysed by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectroscopy and gave signals corresponding to the starting materials<sup>194, 195</sup>.

#### 5.6.2.2-Synthesis of bis-(trimethylsilyl)methylbenzene and reaction with benzaldehyde.



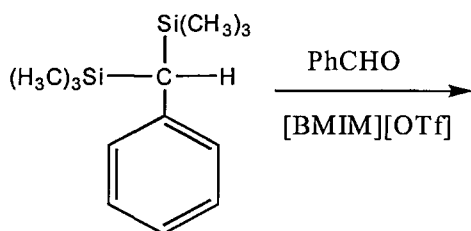
Magnesium (25 g, 1.04 mol) was reacted with trimethylchlorosilane (90 g, 0.82 mol) in dry THF (400 ml) in a three-necked flask. Dichloromethylbenzene (50 g, 0.4 mol) in THF (100 ml) was added to the solution through a dropping funnel. After addition (2 h), trimethylchlorosilane (30 g) was added to the mixture which was then refluxed for 1 h and poured onto crushed ice. The



remaining magnesium was filtered off and the filtrate neutralised with sodium bicarbonate. The organic layer was washed with water and dried over sodium sulfate. The solvent was removed by rota-evaporator. Methanol (150 ml) was chilled to the temperature of a dry ice/acetone mixture and added to the organic layer. The precipitate, which had formed, was removed by filtration and recrystallized from 150 ml of 75 % methanol-25 % ethanol. The product was purified by column chromatography, analysed by NMR spectroscopy and compared with the literature value<sup>196</sup>.

**bis-(Trimethylsilyl)methylbenzene:**  $\delta_H$  (300 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 0.011 (18H, s,  $2 \times Si(CH_3)_3$ ), 1.46 (1H, s,  $SiCHPh$ ), 6.88-7.2 (5H, m, Ph);  $\delta_C$  (75 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 0.34 ( $Si(CH_3)_3$ ), 29.34 ( $SiCHPh$ ), 123.04, 127.83, 128.52, 142.93 ( $4 \times C$  aromatic);  $\delta_{Si}$  (79 MHz,  $CDCl_3$ ,  $Me_4Si$ ) 1.61.

5.6.2.3 Attempted reaction of bis-(trimethylsilyl)methylbenzene with benzaldehyde in [BMIM][OTf]



bis-(Trimethylsilyl)methylbenzene (1 g, 4.23 mmol) was mixed with [bmim][OTf] (5 ml) and benzaldehyde (0.45 g, 4.24 mmol) was added to the mixture and stirred for 24 h at room temperature. The mixture was analysed by  $^1H$ ,  $^{13}C$  and  $^{29}Si$  NMR spectroscopy and only gave signals corresponding to the starting materials<sup>197</sup>.

## Further work

In this thesis we achieved the reduction of aldehydes using hydrosilanes and nucleophiles; under suitable conditions the reaction gave only mixed ethers as product and provided an alternative to the Williamson syntheses. Studies of the hydrosilylation of alkenes showed that different products and isomer ratios are obtained using conventional organic media compared with ionic liquids. Ionic liquid encourages the formation of the  $\alpha$ - product.

The Peterson reaction in ionic liquids was not successful with only starting material being recovered.

With regard to the hydrosilylation of a carbonyl group, it will be interesting to use other types of catalyst such as transition metal complexes, for example  $\text{TiCl}_4$ , which was used in the Sakurai-Hosomi reaction. The reaction could be carried out in organic solvent (particularly DCM) and ionic liquids and the outcome of product obtained, together with quantitative results, compared for both cases.

Also, future studies could be performed on the hydrosilylation of alkenes by screening existing transition metal catalysts and comparing the ratio  $\alpha:\beta$  obtained in organic solvent and ionic liquids.

Due to the lack of time the Peterson reaction was not investigated enough to give appreciable results. Only one example was studied in which benzaldehyde reacted with benzylbis(trimethylsilane) in  $[\text{bmim}][\text{OTf}]$ . Further work could investigate the formation

of olefins in ionic liquids by changing the aldehyde and silane used, and also by working on different conditions for the reaction (reflux, addition of a base etc).

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# Annex

### List of reagents/ purity/ source

Acetophenone	99	ACROS ORGANICS
Allylbenzene	98	Sigma-Aldrich
Allyl butyl ether	98	Sigma-Aldrich
Allyl phenyl ether	99	Sigma-Aldrich
Allylvinylsilane	97	ABCR chemicals
Benzaldehyde	98	ACROS ORGANICS
Benzophenone	99	ACROS ORGANICS
Benzyltriethoxysilane	97	ABCR chemicals
Bromide polymer amberlyst	98	ACROS ORGANICS
Bromine	99	ACROS ORGANICS
Bromobutane	99	ACROS ORGANICS
Butanal	99	ACROS ORGANICS
But-3-enoic acid	97	Sigma-Aldrich
Chloride polymer amberlyst	98	ACROS ORGANICS
Chlorovinyltrimethylsilane	97	ABCR chemicals
Cyclohexane	99	ACROS ORGANICS
Dichloromethylbenzene	98	Sigma-Aldrich
Dimethyldiethoxysilane	97	ABCR chemicals
Dimethylchlorosilane	98	ACROS ORGANICS
Hexanal	98	ACROS ORGANICS
Hexafluorophosphoric acid	60% solution in water ACROS ORGANICS	
1-Hexene	97	ACROS ORGANICS
Hexylacrylate	98	Sigma-Aldrich
Hexyltriethoxysilane	97	Sigma-Aldrich
Lithiotrifluoromethanesulfonimide	97	Sigma-Aldrich
2-Methylbutanal	95	ACROS ORGANICS
Methyldimethoxysilane	99	ABCR chemicals
1-Methylimidazole	98	ACROS ORGANICS
Octanal	98	ACROS ORGANICS
Phenyldimethylsilane	97	ABCR chemicals
Phenyltriethoxysilane	98	ABCR chemicals
Sodium tetrafluoroborate	98	Sigma-Aldrich
Styrene	99	ACROS ORGANICS
Trimethylacetaldehyde	80	ACROS ORGANICS
Tetrabutylammonium bromide	99	ACROS ORGANICS
Tetrabutylammonium chloride	99	ACROS ORGANICS
Tetrabutylammonium iodide	98	ACROS ORGANICS
Tetrabutylammonium triflate	99	Sigma-Aldrich
Tetramethyldisilazane	96	Sigma-Aldrich
Triethoxysilane	97	ABCR chemicals
Triethylsilane	99	ABCR chemicals
Trifluoromethanesulphonic acid	98	Lancaster
Trimethoxycyclopentylsilane	97	ABCR chemicals
Trimethylchlorosilane	98	ABCR chemicals
Trimethylvinylsilane	95	ABCR chemicals

## NMR of known products

**Benzyl alcohol:**  $\delta_{\text{H}}$  (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 2.58 (1H, t,  $^3J=7$  Hz, OH), 3.8 (2H, d,  $^3J=7$  Hz,  $\text{CH}_2$ ) and 7.2-8.5 (5H, m, Ph);  $\delta_{\text{C}}$  (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 35.7 ( $\text{CH}_2\text{OH}$ ), 128-135 (Ph)

**Benzyl butyl ether:**  $\delta_{\text{H}}$  (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.75 (3H, t,  $^3J=6.4$  Hz,  $\text{CH}_3$ ), 1.22 (2H, m,  $\text{CH}_2$ ), 1.44 (2H, m,  $\text{CH}_2$ ), 3.31 (2H, t,  $^3J=6.58$  Hz,  $\text{OCH}_2$ ), 4.36 (2H, s,  $\text{OCH}_2$ ) and 7.2-7.6 (Ph);  $\delta_{\text{C}}$  (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 13.88 ( $\text{CH}_3$ ), 19.34 ( $\text{CH}_2$ ), 31.81 ( $\text{CH}_2$ ), 70.16 ( $\text{OCH}_2$ ), 72.8 ( $\text{OCH}_2$ ), 128.51, 128.66, 137.44 and 138.69.

**Benzyl (2,2-dimethylpropyl) ether:**  $\delta_{\text{H}}$  (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.9 (9H, s,  $3\times\text{CH}_3$ ), 3.2 (2H, s,  $\text{OCH}_2$ ), 4.1 (2H, s,  $\text{OCH}_2$ ), 7.2-7.5 (5H, m, Ph);  $\delta_{\text{C}}$  (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 26.8 ( $\text{CH}_3$ ), 32.5 ( $\text{CMe}_3$ ), 72.1 ( $\text{OCH}_2$ ), 81.9 ( $\text{OCH}_2$ ), 127.75, 128, 128.6 and 138.5 .

**Benzyl hexyl ether:**  $\delta_{\text{H}}$  (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.89 (3H, t,  $^3J=6.61$  Hz,  $\text{CH}_3$ ), 1.26 (8H, m,  $4\times\text{CH}_2$ ), 3.6 (2H, t,  $^3J=6.6$  Hz,  $\text{OCH}_2$ ), 4.5 (2H, s,  $\text{OCH}_2\text{Ph}$ ) and 7.2-7.7 (5H, m, Ph);  $\delta_{\text{C}}$  (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 14.06 ( $\text{CH}_3$ ), 24.31 ( $\text{CH}_2$ ), 28.72 ( $\text{CH}_2$ ), 32.94 ( $\text{CH}_2$ ), 37.58 ( $\text{CH}_2$ ), 70.84 ( $\text{OCH}_2$ ), 71.49 ( $\text{OCH}_2\text{Ph}$ ), 125-142 (4C aromatic).

**Benzyl octyl ether:**  $\delta_{\text{H}}$  (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 0.93 (3H, t,  $^3J=7$  Hz,  $\text{CH}_3$ ), 1.26 (10H, m,  $5\times\text{CH}_2$ ), 1.64 (2H, m,  $\text{CH}_2$ ), 3.66 (2H, t,  $^3J=6.8$  Hz,  $\text{OCH}_2$ ), 4.47 (2H, s,  $\text{OCH}_2\text{Ph}$ ) and 7.2-7.7 (5H, m, Ph);  $\delta_{\text{C}}$  (75MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 14.16 ( $\text{CH}_3$ ), 23.87 ( $\text{CH}_2$ ), 28.27 ( $\text{CH}_2$ ), 33.08 ( $\text{CH}_2$ ), 36.5 ( $\text{CH}_2$ ), 71.38 ( $\text{OCH}_2$ ), 71.69 ( $\text{OCH}_2\text{Ph}$ ), 125-142 (Ph).

**Bicyclohexyliden-2-one:**  $\delta_{\text{H}}$  (300MHz,  $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ) 2.29 (2H, t,  $^3J=6.6\text{Hz}$ ,  $\text{COCH}_2$ ), 2.09 (2H, t,  $^3J=6.9\text{Hz}$ ,  $\text{CH}_2$ ), 1.83 (4H, t,  $^3J=6.9\text{Hz}$ ,  $2\times\text{CH}_2$ ), 1.77 (2H, m,  $\text{CH}_2$ ), 1.66 (2H, m,  $\text{CH}_2$ ), 1.24 (4H, m,  $2\times\text{CH}_2$ ) and 1.19 (2H, t,  $^3J=6.9\text{Hz}$ ,  $\text{CH}_2$ );  $\delta_{\text{C}}$  (75MHz,  $\text{CDCl}_3$ ,

Me<sub>4</sub>Si) 211.7 (CO), 129.42 (=C), 127.7 (C=), 69.7 (C6), 41.4 (C3), 35 (C8), 26.5 (C5), 24.9 (C4), 24.5 (C9) and 23.6 (C10).

**bis-(2,2-Dimethylpropyl) ether:**  $\delta_H$  (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.91 (27H, s, 9×CH<sub>3</sub>), 2.95 (4H, s, 2×OCH<sub>2</sub>);  $\delta_C$  (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 26.51 (CH<sub>3</sub>), 32.1 (CMe<sub>3</sub>) and 81.63 (OCH<sub>2</sub>).

**bis-(2-Methylbutyl) ether:**  $\delta_H$  (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.84 (6H, d,  $^3J=7.3$  Hz, 2×CH<sub>3</sub>), 0.9 (6H,  $^3J=7.3$  Hz, d, 2×CH<sub>3</sub>), 1.35 (2H, m, CH), 1.4 (4H, m, CH<sub>2</sub>) and 3.12 (4H, d,  $^3J=8.2$  Hz, OCH<sub>2</sub>);  $\delta_C$  (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 13.8 (CH<sub>3</sub>), 14.7 (CH<sub>3</sub>), 21.3 (CH), 25.4 (CH<sub>2</sub>) and 73.61 (OCH<sub>2</sub>).

**Butanol:**  $\delta_H$  (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.87 (3H, t,  $^3J=7$ Hz, CH<sub>3</sub>), 1.4-1.6 (4H, m, 2×CH<sub>2</sub>), 2.85 (1H, t,  $^3J=6.7$ Hz) and 3.45 (2H, m, CH<sub>2</sub>OH);  $\delta_C$  (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 13.18 (CH<sub>3</sub>), 17.2 (CH<sub>2</sub>), 33.7 (CH<sub>2</sub>) and 62.5 (CH<sub>2</sub>OH).

**Butoxy(dimethyl)silane:**  $\delta_H$  (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.19 (6H, d,  $^3J=3.3$ Hz, 2×SiCH<sub>3</sub>), 0.68 (3H, t,  $^3J=6.9$ Hz, CH<sub>3</sub>), 1.09 (2H, m,  $^3J=6.6$ Hz, CH<sub>2</sub>), 1.32 (2H, m,  $^3J=6.9$ Hz, CH<sub>2</sub>), 3.42 (2H, t,  $^3J=7$ Hz, OCH<sub>2</sub>) and 4.42 (1H, m,  $^3J=3$ Hz, Si-H);  $\delta_C$  (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) : 1.44 (SiCH<sub>3</sub>), 14.05 (CH<sub>3</sub>), 22.5 (CH<sub>2</sub>), 28.31 (CH<sub>2</sub>), 35.97 (CH<sub>2</sub>) and 70.13 (OCH<sub>2</sub>);  $\delta_{Si}$  (79.3MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) -3.6.

**Butyl (2,2-dimethylpropyl) ether:**  $\delta_H$  (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.95 (9H, s, 3×CH<sub>3</sub>), 1.1 (3H, t, CH<sub>3</sub>), 1.53 (4H, m, 2×CH<sub>2</sub>), 3.05 (2H, s, OCH<sub>2</sub>), 3.6 (2H, t,  $^3J=7$  Hz, OCH<sub>2</sub>);  $\delta_C$  (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 15.1 CH<sub>3</sub>), 23.91 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 26.6 (CH<sub>3</sub>), 36.87 (CH<sub>2</sub>), 32.24 (CMe<sub>3</sub>), 71.8 (OCH<sub>2</sub>) and 81.7 (OCH<sub>2</sub>).

**Butyl octyl ether:**  $\delta_H$  (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.87 (3H, t,  $^3J=6.97$  Hz, CH<sub>3</sub>), 0.89 (3H, t,  $^3J=7.3$  Hz, CH<sub>3</sub>), 1.46 (12H, m, 6×CH<sub>2</sub>), 1.53 (4H, m, 2×CH<sub>2</sub>), 3.35 (2H, t,  $^3J=6$  Hz,

OCH<sub>2</sub>) and 3.41 (2H, t, <sup>3</sup>J=5.9 Hz, OCH<sub>2</sub>); δ<sub>C</sub> (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 13.58 (CH<sub>3</sub>), 14.07 (CH<sub>3</sub>), 19.34(CH<sub>2</sub>), 19.65(CH<sub>2</sub>), 20.23(CH<sub>2</sub>), 20.67(CH<sub>2</sub>), 20.88(CH<sub>2</sub>), 22.67(CH<sub>2</sub>), 31.81 (CH<sub>2</sub>), 34.1 (CH<sub>2</sub>), 70.16 (OCH<sub>2</sub>) and 72.8 (OCH<sub>2</sub>).

**Dibenzhydryl ether:** δ<sub>H</sub> (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.7 (2H, s, OCH) and 7.2-7.5 (20H aromatic, m, 4×Ph); δ<sub>C</sub> (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 69.7 (OCH), 124.9, 126.5, 127.3 and 139.8.

**Dibenzyl ether:** δ<sub>H</sub> (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.52 (2H, s, 2×CH<sub>2</sub>), 7.17-7.45 (5H, m, 2×Ph); δ<sub>C</sub> (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 72.06 (OCH<sub>2</sub>), 127.68, 127.91, 128.31 and 138.21.

**Dibutyl ether:** δ<sub>H</sub> (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.05 (6H, <sup>3</sup>J=6.8 Hz, t, CH<sub>3</sub>), 1.48 (8H, m, 2×CH<sub>2</sub>), 3.49 (4H, <sup>3</sup>J=6.6 Hz, t, OCH<sub>2</sub>); δ<sub>C</sub> (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.95 (CH<sub>3</sub>), 28.58 (CH<sub>2</sub>), 36.52 (CH<sub>2</sub>) and 71.33 (OCH<sub>2</sub>).

**Dihexyl ether:** δ<sub>H</sub> (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.25 (3H, t, <sup>3</sup>J=6.7 Hz, CH<sub>3</sub>), 1.41 (6H, m, 3×CH<sub>2</sub>), 1.67 (2H, m, CH<sub>2</sub>) and 3.55 (2H, t, <sup>3</sup>J=6.57 Hz, OCH<sub>2</sub>); δ<sub>C</sub> (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 15.22 (CH<sub>3</sub>), 24.95 (CH<sub>2</sub>), 29.08 (CH<sub>2</sub>), 33.75 (CH<sub>2</sub>), 38.4 (CH<sub>2</sub>) and 71.66 (OCH<sub>2</sub>).

**Dimethyl(dibenzoyloxy)silane:** δ<sub>H</sub> (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.64 (6H, s, 2×SiCH<sub>3</sub>), 3.44 (2H, s, SiOCH<sub>2</sub>Ph) and 7.4-7.6 (5H, m, Ph); δ<sub>C</sub> (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.55 (SiCH<sub>3</sub>), 58.1 (OCH<sub>2</sub>), 127.54 (C4), 127.86 (C3), 128.17 (C2) and 136.57 (C1).<sup>57</sup>

**Diocetyl ether:** δ<sub>H</sub> (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si); 0.78 (3H, <sup>3</sup>J= 6.61 Hz, t, CH<sub>3</sub>), 1.23-1.5 (12H, m, 6×CH<sub>2</sub>) and 3.62 (2H, <sup>3</sup>J= 6.61 Hz, t, CH<sub>2</sub>O); δ<sub>C</sub> (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 14.05 (CH<sub>3</sub>), 22.6-33.25 (6×CH<sub>2</sub>) and 70.93 (CH<sub>2</sub>O).

**Diphenethyl ether:** δ<sub>H</sub> (300MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 3.7 (4H, t, <sup>3</sup>J=7 Hz, 2×CH<sub>2</sub>), 4.8 (4H, t, <sup>3</sup>J= 7Hz, 2×OCH<sub>2</sub>) and 7.3-7.5 (10H, m, 2×Ph); δ<sub>C</sub> (75MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 36.86 (CH<sub>2</sub>), 63.9 (OCH<sub>2</sub>) and 126.7-137.8 (Ph).

**1,3 Diphenylbut-2-en-1-one :**  $\delta_H$  (300MHz,  $CDCl_3$ ,  $Me_4Si$ ) 2.57 (3H, d,  $^4J=1.2$  Hz,  $CH_3$ ), 7.02 (1H, q, =CH) and 7.8-7.2 (10H aromatic, m,  $2\times Ph$ );  $\delta_C$  (75MHz,  $CDCl_3$ ,  $Me_4Si$ ) 33.9 ( $CH_3$ ), 124.8, 126.2, 128.12, 128.5, 132.5 (=C), 136.6 (COC=) and 201(CO).

**Diphenylmethane:**  $\delta_H$  (300MHz,  $CDCl_3$ ,  $Me_4Si$ ) 4.21(2H, s,  $CH_2$ ) and 7-7.5 (10H aromatic, m,  $2\times Ph$ );  $\delta_C$  (75MHz,  $CDCl_3$ ,  $Me_4Si$ ) 41.1 ( $CH_2$ ), 140.2, 126.3, 128.9 and 128.5.

**Hexyloxy(dimethyl)silane:**  $\delta_H$  (300MHz,  $CDCl_3$ ,  $Me_4Si$ ) 0.09 (6H, d,  $^3J=3.3$ Hz,  $2\times SiCH_3$ ), 0.71 (3H, t,  $^3J=6.9$ Hz,  $CH_3$ ), 1.14-1.35 (6H, m,  $^3J=6.6$ Hz,  $3\times CH_2$ ), 1.65 (2H, m,  $^3J=6.6$ Hz,  $CH_2$ ), 3.43 (2H, t,  $^3J=7$ Hz,  $OCH_2$ ) and 4.42 (1H, m,  $^3J=2.7$ Hz, Si-H);  $\delta_C$  (75MHz,  $CDCl_3$ ,  $Me_4Si$ ) : 1.44 ( $SiCH_3$ ), 14.21 ( $CH_3$ ), 22.5 ( $CH_2$ ), 28.31 ( $CH_2$ ), 39.5 ( $CH_2$ ), 35.97 ( $CH_2$ ) and 70.13 ( $OCH_2$ ).  $\delta_{Si}$  (79.3MHz,  $CDCl_3$ ,  $Me_4Si$ ) -2.9.

**Octanol:**  $\delta_H$  (300MHz,  $CDCl_3$ ,  $Me_4Si$ ) 0.87 (3H, t,  $^3J=6.4$  Hz,  $CH_3$ ), 1.2-1.6 (12H, m,  $6\times CH_2$ ), 2.32 (1H, t,  $^3J=6.9$  Hz, OH) and 3.41 (2H, m,  $CH_2OH$ );  $\delta_C$  (75MHz,  $CDCl_3$ ,  $Me_4Si$ ) 12.5 ( $CH_3$ ), 20.6-30 ( $6\times CH_2$ ) and 65.7 ( $CH_2OH$ ).

**t-Butoxy(dimethyl)silane:**  $\delta_H$  (300MHz,  $CDCl_3$ ,  $Me_4Si$ ) 0.15 (6H, d,  $^3J=3.3$ Hz,  $2\times SiCH_3$ ), 0.54 (9H, s,  $3\times CH_3$ ), 4.45 (1H, sept,  $^3J=2.7$ Hz, Si-H);  $\delta_C$  (75MHz,  $CDCl_3$ ,  $Me_4Si$ ) : 0.8 ( $SiCH_3$ ), 11.6 ( $CH_3$ ), 11.79 ( $CH_3$ ), 11.86 ( $CH_3$ ) and 32.7 ( $C(CH_3)_3$ ).